INTERNATIONAL ATOMIC WEIGHTS, 1915

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Beryllium	Be	9.1	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Cæsium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium		
Lutecium	Lu	174.0	(Neoytterbium)	Yb	172.0
Magnesium	Mg	24.32	Yttrium	Yt	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6

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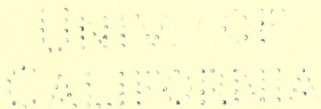2006

SYNTHETIC
INORGANIC CHEMISTRY

A LABORATORY COURSE FOR
FIRST YEAR COLLEGE STUDENTS

BY

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SECOND EDITION, WITH SUPPLEMENT
FOURTH THOUSAND

PREFACE

THIS series of notes was designed to serve as a guide for laboratory work and study in Inorganic Chemistry during the second term of the first year at the Massachusetts Institute of Technology. It had been felt for some time that Qualitative Analysis, which was previously made the basis for laboratory practice during that period, did not fully meet the requirements and that a course based upon the actual preparation of typical chemical substances might prove more satisfactory. In consequence, notes in essentially the form now published were prepared during the year 1906–07, they being the direct outcome of several years' previous trial of a limited amount of preparation work with the classes. The present book is a thorough revision of those notes in the light of experience in their actual application.

During the first term's study of chemistry there can be little doubt that a course of simple experiments, such as has long been in use, in the methods of formation and in the study of the properties of the non-metallic elements — oxygen, hydrogen, the halogens, sulphur, nitrogen, and carbon — and their compounds, is the most satisfactory. But when it comes to the study of the metallic elements, three options as to laboratory work present themselves: First, a continuation of experiments similar in nature to those of the first term; second, Qualitative Analysis; third, Preparation Work. The disadvantages of the first plan are that the experiments are so quickly performed and so alike in character that they fail to arouse much enthusiasm in the student or to leave very vivid impressions on his mind. Qualitative analysis is in many ways a most excellent basis for teaching the chemistry of the metallic elements; but its chief disadvantages are: First, that it is one-sided, it dealing as it does

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almost exclusively with the chemistry of solutions and the formation of highly insoluble bodies ; second, that it requires the sequence followed in the lectures to be that of the qualitative procedure instead of a more natural one based on the periodic classification ; and third, that it is well-nigh impossible to keep from the student's mind the false idea that the end and aim of qualitative analysis is principally "to get the unknowns correct."

Some of the advantages which seem to be possessed by a course of preparation work such as outlined in the following pages are :

1. The sequence of the exercises may follow that of the lectures.

2. Very varied types of chemical change are illustrated, both those in the furnace and those in solution. In solution advantage is taken not only of high degrees of insolubility, but also of differences in solubility among the more soluble bodies as well as of differences in the effect of temperature on solubility.

3. The danger of the work becoming a mechanical following of directions is reduced by the introduction of study questions and experiments with each exercise.

4. In its effect in awakening the student's interest this line of work has proved particularly successful, — the making of preparations is, in fact, in its very nature one of the most fascinating forms of chemical work. Since each preparation requires a good deal of time and thought, and the product when obtained is something definite and tangible, the knowledge thus gradually absorbed is more definite and less easily forgotten than when the laboratory work consists of a large number of test tube reactions.

After the completion of such a course as this, if the student commences analytical work with some conception of the sources and methods of obtaining the substances

which he is to use as reagents, etc., there can be no doubt that the latter work will then have a much deeper meaning.

The plan kept in mind in preparing this course is, briefly, as follows: The greater part of the preparations selected are of industrial importance, and for the starting point of each either natural products or crude manufactured materials are used so far as is possible. The course does not aim to be an exhaustive one in chemical preparations, but a limited number of exercises are selected to illustrate the most important types of compounds of the common elements and the most important methods. Two or three times as many exercises are furnished as any one student will be able to complete in the time usually allotted; thus different students may be assigned different preparations.

The notes for each exercise are divided into three parts: I. A discussion of the object of the exercise, with an outline of the principle of the method and the reasons for the steps involved. II. Working directions which, if carefully followed, should result in obtaining a satisfactory product. It is believed far better to make the directions very explicit, for the reason that the inexperienced student may easily become discouraged by failures due to difficulties which he is unable to foresee. Difficulties enough are sure to arise to develop originality and resourcefulness. III. Questions for study which involve additional laboratory experiments, the consulting of text-books, and original reasoning.

At the end of each group of exercises is furnished a set of general study questions, and this arrangement of the exercises in groups is such as to bring out the relationships shown in the periodic classification of the elements.

In the discussions and questions given with the various exercises it is assumed that the student has an elementary knowledge of the electrolytic dissociation theory and of the principle of mass action. In the opinion of the author

a great opportunity is lost for bringing out relationships among chemical phenomena if these principles are not taught during the first term's study of college chemistry and their applications pointed out in connection with later work in inorganic preparations and in analytical chemistry. The effort has been to make the questions such as cannot be answered mechanically. Some of the questions may, in consequence, seem rather difficult and incapable of direct answers; the object of the questions is, however, not solely to bring forth correct statements of facts and theories, but is also to teach the student to use his head in seeking for the significance of facts and in reasoning from one fact to another.

Acknowledgment is due to many sources for the outline of the greater part of the methods given. The details of all of them have, however, been very carefully worked over and adapted for the purpose in view.

In conclusion the author wishes to express his sense of obligation to Professor Henry P. Talbot, head of the Department of Chemistry, at whose request the preparation of these notes was undertaken; also to other members of the instructing staff at the Massachusetts Institute of Technology for helpful criticism and suggestions, and particularly to Mr. J. W. Phelan, to whose efficient management of the laboratory instruction is due any success with which this course has met at this Institute.

This little book is presented for publication with the desire to offer for the consideration of those in charge of the instruction at other institutions a plan of first-year work which has quite new and perhaps advantageous features. It is hoped that it may do its part in securing recognition of the importance of synthetic or preparative work in a well-balanced course of chemical training.

ARTHUR A. BLANCHARD.

March, 1908.

PREFACE TO SECOND EDITION

THE plan of work embodied in the first edition has remained unchanged in the second edition, but many minor improvements have been made and considerable new material has been added.

Several of the procedures have been altered, so that good results may be more confidently expected from inexperienced students. A few new preparations have been added to the list in order to include important types of processes which were not well represented in the first edition. The general questions following each group of exercises have been entirely rewritten, and now present a more consistent plan to bring out the main characteristics of the various groups and the relations among the groups. The number of these questions has been considerably reduced, and it is now felt even more strongly than before that all of the general questions should be mastered by every student who takes the course. For the convenience of teachers as well as of enthusiastic students, a number of additional general questions have been placed in the appendix. An introductory section has been included, explaining principles and details of laboratory manipulation. A new chapter (Chapter VII) has been added, which embraces the non-metallic elements, and is intended to recall and to broaden the knowledge which the student was supposed to possess before commencing the study of the metallic elements. Some useful tables have been added in the appendix, and a few cuts have been inserted in the text.

June, 1910.

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SYNTHETIC INORGANIC CHEMISTRY

Introductory to the Student

THE following exercises are designed to illustrate the principles and methods involved in the preparation of a number of the most important chemicals. Where possible the method employed resembles that actually used on an industrial scale; where this is, however, impossible on the limited scale of the laboratory, mention is made of the fact, with reasons therefor. On account of the limitations connected with work on a laboratory scale, it is of course impossible to get as high percentage yields as could be obtained on a large commercial scale. The amounts obtained of each preparation are to be weighed and recorded, but the chief stress is to be laid upon the excellence of the product rather than upon its quantity.

A larger number of preparations is given than it is expected that the student can accomplish in fifteen weeks with but four hours per week in the laboratory. Each student, therefore, will be assigned certain of the exercises which he is expected to thoroughly master, and which he is expected to perform *entirely independently*. But almost equal in importance is it for him to know the work which the students about him in the laboratory are performing. To this end it is important that the directions, and more especially the first sections which discuss the principles involved, be studied for each exercise, and then that the work of neighboring students actually at work upon the preparations be observed and discussed with them in

the odd moments which will invariably occur when waiting for evaporations or filtrations to take place.

Directions for laboratory work: The notes for each preparation are divided into three parts:

I.   Discussion of the general principles involved.

II. Directions for actual manipulation.

III. Study questions.

Part I is to be read and understood before commencing work in the laboratory.

Part II, being the working directions, is to be kept at hand while carrying out the manipulations. These directions do not need to be recorded in the laboratory note-book; but it is essential, nevertheless, to keep a laboratory notebook in which to enter all important observations and data; such as, for example, appearance of solutions (color, turbidity); appearance of precipitates or crystals (color, size of grains, crystalline form); results of all weighings or measurements; number of recrystallizations; results of tests for purity of materials, etc.

Part III constitutes directions for study based upon the particular preparation. This will involve: (1) laboratory experiments and direct entries in the laboratory note-book; (2) consultation of reference books, of which all that are necessary will be found upon the shelf in the laboratory; (3) original reasoning.

The answers to the questions should be written in the laboratory notebook following the entries for the exercise, and this book should be submitted at the same time as the preparation for the approval of an instructor.

Besides the specific study questions for each preparation there are, accompanying each group of exercises, general questions relating to the whole group; and these are to be worked out by every student. The answers to these questions are to be written on a certain prescribed

kind of paper and handed in at the office, neatly bound, within the times which will be posted.

In preparation work it is frequently necessary to wait for considerable periods of time for evaporations, crystallizations, etc., to take place. This time may be utilized for work upon the study questions and experiments, but even then it is advisable to have usually more than a single preparation under way. Thus no time need be wasted by the energetic student who plans his work well.

NOTES ON LABORATORY MANIPULATION

THESE notes are intended simply to help the student in foreseeing and in overcoming some of the difficulties that arise in experimental work. They by no means make it unnecessary for him to exercise ingenuity and originality in planning and carrying out the details of laboratory work. At the outset these notes should be read through carefully; then when in the later work references to specific notes are made their general bearing will be better appreciated.

1. PRECIPITATION; CRYSTALLIZATION

In the majority of chemical processes which are carried out in the *wet way*, separations are accomplished by taking advantage of differences in solubility. In case a certain product is extremely insoluble and is formed almost instantaneously when solutions containing the requisite components are mixed, the process is called *precipitation* and the insoluble substance is called the *precipitate*. If the product to be formed is less insoluble, so that it separates more slowly, or only after evaporating away a part of the solvent, the process is called *crystallization*.

In some cases the precipitate, or the crystals, constitute the desired product; in other cases a product which it is necessary to remove from the solution before the desired product can be obtained pure. In either case it is necessary to make as complete a separation as possible of the solid from the liquid. This involves the manipulations described under Notes 2, 3, and 4.

2. POURING

In pouring a liquid from a vessel, either into a filter or into another vessel, care must be taken not to slop the liquid nor to allow it to run down the outside of the vessel poured from. To this end touch a stirring rod to the lip of the
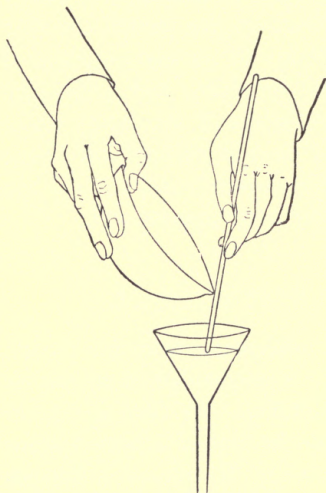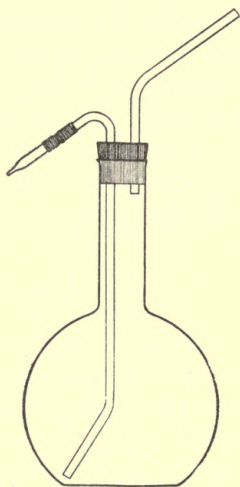
FIG. 1   FIG. 2

dish or beaker (Fig. 1) and allow the liquid to run down the rod.

3. TRANSFERRING PRECIPITATES OR CRYSTALS

If large crystals have separated from a liquid they may be picked out, or the liquid may be poured off.

If a precipitate or a crystalline meal has formed it must be drained in a filter funnel. First pour off the liquid (see Note 2) — through the filter if necessary, so as to save any

floating particles of the solid — then pour the main part of the damp solid into the filter. A considerable part of the solid will adhere to the dish; most of this may be scraped out by means of a spatula, but the last of it is most easily *rinsed* into the filter. For rinsing, a jet of water from the wash bottle (Fig. 2) may be used if the solid is very insoluble. If the solid is soluble in water, some of the saturated solution may be poured back into the dish from out of the filter bottle, and by means of this the last of the solid may be removed to the filter.

4. FILTERING; COLLECTING PRECIPITATES

(*a*) *A coarse-grained crystal meal* can best be collected in a filter funnel in which a perforated porcelain plate is placed, and the mother liquor clinging to the crystals can best be removed with the aid of suction (see next paragraph).
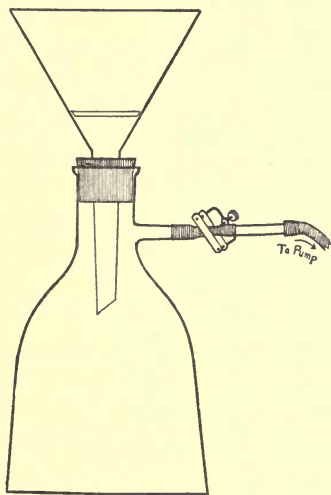
(*b*) *Filtering with Suction; Witt Filter.* — With a fine-grained crystal meal, or a precipitate which is not of such a slimy character as to clog the pores of the filter paper, a Witt filter is most advantageously used. For most general use a 5-inch filter funnel should be fitted tightly by means of a rubber stopper into the neck of a 500 cc. filter bottle (Fig. 3). Place a 1½-inch perforated filter plate in the

FIG. 3

funnel and on this a disk of filter paper cut so that its edges will turn up about 3 mm. on the side of the funnel all the way around.   Hold the disk of dry paper in the right position, wet it with a jet from the wash bottle, draw it firmly down against the filter plate by applying the suction, and press the edges firmly against the side of the funnel, so that no free channel shall remain.   In pouring the liquid, direct it with a stirring rod (Note 2) onto the middle of the filter ; do not allow it to run down the side of the funnel, as this might turn up the edge of the paper and allow some of the precipitate to pass through. After bringing all of the solid upon the filter it may be freed from a large part of the adhering liquid by means of the suction, and it may then be purified by washing with a suitable liquid (see Note 5).

The Witt filter is very generally useful for the purpose of separating a solid product from a liquid.   In cases that the liquid runs slowly, the rate of filtration can be increased by using a larger filter plate or still better a Büchner funnel and thereby increasing the filtering area.   The student should, however, avoid using the suction indiscriminately, for in many cases it is, as explained in paragraph c, a positive disadvantage.

Suction. — The most convenient source of suction is the Richards water pump, which can be attached directly to the water tap.   If the water is supplied at a pressure of somewhat over one atmosphere (34 feet of water), a vacuum of very nearly an atmosphere can be obtained.   If the pressure is insufficient, an equally good vacuum can be obtained by means of the suction of the escaping water.   To this end the escape pipe must be prolonged by a tube sufficiently constricted to prevent the sections of the descending water column from breaking and thus allowing air to enter from the bottom.

To keep the suction pump working continuously, however, is extravagant of water as well as being a nuisance in the laboratory on account of the unnecessary noise. Consequently this rule is made and must be observed:

The suction pump must never be kept in operation more than two minutes at one time.

If suction must be applied for more than that length of time, the vacuum which is produced inside of the two minutes may be maintained in the suction bottle by closing the latter air tight. For this purpose the bottle is to be fitted as follows:

Connect a short piece of rubber tube with the side arm of the filter bottle. Provide this tube with a screw cock and connect its further end with a short piece of glass delivery tube tapered a little at each end and rounded in the flame. (See Fig. 3 on page 7.)

The short glass tube can be attached to and removed from the pump at will, and a vacuum once produced in the bottle can be preserved by closing the screw cock. Thus, for example, if all the joints of the bottle are tight, a slimy precipitate may be left filtering under suction over night or even longer.

(*c*) *Filtering without Suction.* — A slimy or gelatinous precipitate can be collected much better without suction. Suction drags the solid matter so completely into the pores of the filter that in most cases the liquid nearly ceases to run. A filter funnel and filter should be chosen large enough to hold the entire precipitate. The filter paper should be folded twice and then opened out in the form of a cone and fitted into the funnel (Instructions). The corners of the filter should be cut off round, and the upper edge of the filter should come about one-half inch below the rim of the funnel. It is usually best to fit the paper carefully into the funnel, to wet it and press it up

against the glass all around, so that there will be no air channels.

In the case of slow-running liquids, if a large filter is used, it may be filled at intervals and left to take care of itself the rest of the time while other work is being done.

In case a considerable weight of liquid is to come on the point of the filter, this may be reënforced by means of a piece of linen cloth, which should be placed under the middle of the filter paper before it is folded, and should then be folded in with it so as to strengthen the point.

After the precipitate is collected in the filter and drained, it should if necessary be washed (see Note 5 on page 12).

Both filtration and washing take place much more rapidly if the liquid is hot. Time can also usually be saved if the precipitate is allowed to settle as completely as possible before commencing to filter. The clear liquid can then be decanted off, or if necessary poured rapidly through the filter before the latter becomes clogged with the main part of the precipitate.

(*d*) *Filtering Corrosive Liquids.* — Solutions of very strong oxidizing agents, concentrated solutions of the strong acids and bases, and concentrated solutions of a few salts of the heavy metals — notably zinc chloride and stannous chloride — attack filter paper strongly. Ordinary paper is thus entirely unserviceable for filtration, but a felt made of asbestos fibers is in many cases very useful. Shredded asbestos, which has been purified by boiling with hydrochloric acid and subsequent washing, is suspended in water; the suspension is poured onto a perforated plate placed in a filter funnel; and suction is applied whereby the water is removed and the fibers are drawn together to form a compact *felt* over the filter plate. Enough asbestos should be used to make a felt 1 to 3 mm. thick, and care must be taken to see that it is of uniform thickness and that no free

channels are left through which solid matter may be drawn. Before it is ready for use a considerable amount of water should be drawn through the filter, and the loose fibers should be rinsed out of the filter bottle. Before pouring the liquid onto the filter the suction should be started gently, and the liquid should be directed by means of a stirring rod (Note 2) onto the middle of the filter. If these precautions are not observed the felt may become turned up in places, so that the precipitate will pass through.

(*e*) *Cloudy Filtrates.* — When a filtrate at first comes through cloudy, it is usually sufficient to pour the first portion through the filter a second time. The pores of the filter soon become partially closed with the precipitate, so that then even the finest particles are retained.

With some very fine-grained precipitates, repeatedly pouring the filtrate through the same filter will finally give a clear filtrate.

Special kinds of filter paper are made to retain very fine precipitates, but they allow the liquid to pass much more slowly than ordinary filters, and their use is by no means essential in any of the following preparations.

(*f*) *To Keep Liquids Hot during Filtration.* — When liquids must be kept hot during a slow filtration, as, for example, when cooling would cause a separation of crystals that would clog the filter, it sometimes becomes necessary to surround the funnel with a jacket which is heated with steam or boiling water. In the following preparations the use of such a device will not be necessary, although there are several instances where it is necessary to work quickly to avoid clogging the filter.

(*g*) *Cloth Filters.* — In preparations made on a small scale, paper filters placed in ordinary filter funnels are invariably used if the liquid is not too corrosive. On a larger scale or in commercial practice, cloth is much used for fil-

ters, and it can be made in the shape of bags or it can be stretched over wooden frames. The cloth or other filtering medium (asbestos, paper pulp, sand, etc.) has to be chosen in each case with reference to the nature of the precipitate and the corrosiveness of the liquid.

Many of the preparations in this book, if carried out on a larger scale than given in the directions, would require the use of such cloth filters. It is often advantageous to tack one piece of cloth permanently across a wooden support and on top of this to lay a second cloth. The precipitate can then be easily removed together with the unfastened cloth.

For devices for rapid filtration and filtration in general on a large scale, a work on Industrial Chemistry should be consulted.

5. WASHING PRECIPITATES

(*a*) *Washing on the Filter.* — To remove completely the impurities contained in the mother liquor clinging to precipitates or crystals, the solid is washed. Pure water is used for washing, provided the solid is not too soluble or is not decomposed (hydrolyzed) by it. Special directions will be given when it is necessary to use other than pure water.

First, the solid should be allowed to drain as completely as possible, then the wash liquid should be applied, preferably from the jet of a wash bottle, so as to wet the whole mass and to rinse down the sides of the filter. If suction is used, suck the solid as dry as possible, then stop the suction while applying the washing liquid; after the solid is thoroughly wet, suck out the liquid and repeat the washing.

A little thought will make it clear that the washing is much more effective if the liquid is removed as completely

as possible each time before applying fresh wash liquid, and that a number of washings with a small amount of liquid each time is more effective than fewer washings with much greater quantities of wash liquid.   It is, of course, evident that with each washing the liquid should penetrate to all parts of the solid material.

(*b*) *Washing by Decantation.* — In case a precipitate is very insoluble it can be most thoroughly and quickly washed by decantation.   This consists in allowing it to settle in a deep vessel and then in pouring (decanting) or siphoning off the clear liquid.   Following this the precipitate is stirred up with fresh water and allowed to settle, and the liquid is again decanted off.   By a sufficient number of repetitions of this process, the precipitate may be washed entirely free from any soluble impurity, after which it may be thrown on a filter, drained, and then dried.

Most precipitates, even after they have settled as completely as possible in the liquid from which they were thrown down, are very bulky, and their apparent volume is very large as compared with the actual volume of the solid matter itself. For example, a precipitate of basic zinc carbonate (No. 16, page 74), after it has settled as completely as possible in a deep jar (Fig. 4), may still occupy a volume of 400 cc.   When this bulky precipitate is dried, however, it shrivels up into a few small lumps whose total volume is not more than 4 or 5 cc.

If a precipitate, which is at first uniformly suspended in a liquid, is allowed to settle in a tall jar until it occupies but $\frac{1}{5}$ of the original volume
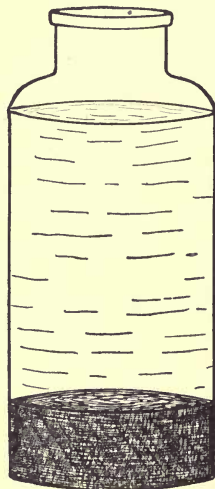
FIG. 4

of the mixture (Fig. 4), any soluble substances will still remain uniformly distributed throughout the whole volume. If now the upper $\frac{4}{5}$, consisting of the clear solution, is drawn away, it follows that practically $\frac{1}{5}$ of the solution, containing $\frac{1}{5}$ of the soluble impurities, remains with the precipitate. By stirring up the solid again with pure water, the soluble impurities become uniformly distributed through the larger volume, and on letting the precipitate settle and drawing off $\frac{4}{5}$ of the liquid, as before, there will remain with the wet precipitate only $\frac{1}{5} \times \frac{1}{5} = \frac{1}{25}$ of the original soluble matter. After the third decantation the remaining suspension will contain $\frac{1}{5} \times \frac{1}{25} = \frac{1}{125}$ of the original impurities, and so on.

6. EVAPORATION

When it is necessary to remove a part of the solvent from a solution, as when a dissolved substance is to be crystallized out, the solution is evaporated. In some cases, where the dissolved substance is volatile or is decomposed by heat, the evaporation must take place at room temperature, but ordinarily in the following preparations the liquid may be boiled. The boiling down of a solution should always be carried out in a porcelain dish of such a size that at the outset it is well filled with the liquid. (Never evaporate in a beaker.) · The flame should be applied directly under the middle of the dish where the liquid is deepest; the part of the dish against which the flame plays directly should be protected with wire gauze. Under no circumstances should the flame be allowed to play up over the sides of the dish : first, because, by heating where the dish is part cooled by liquid and part uncooled, there is great danger of breaking; second, because by heating the sides the film of liquid which creeps up is evaporated and the solid deposited becomes baked hard and in some

cases is decomposed. To prevent the formation of a solid crust around the edges, which even at best will take place to some extent, the dish should occasionally be tilted back and forth a little, so that the crust may be dissolved, or loosened, and washed back into the middle of the dish.

While evaporating a liquid over a flame it should be carefully watched, for if it should be forgotten and evaporate to dryness the dish would probably break and the product be spoiled. If a precipitate or crystals separate from the liquid and collect in a layer at the bottom, the dish will probably break, because where the solid prevents a free circulation of the liquid the dish becomes superheated, and then when in any one place the liquid does penetrate, the sudden cooling causes the porcelain to crack. Usually when a solid begins to separate from a boiling liquid the evaporation should be stopped and the liquid left to crystallize. After that the mother liquor may be evaporated further in a smaller dish.

7. DISSOLVING SOLID SUBSTANCES

The process of dissolving solid substances is hastened, first by powdering the substance as finely as possible, and second by raising the temperature. The solid and solvent should be heated together in a porcelain dish (not in a beaker), and care should be taken to keep the mixture well stirred, for if the solid should settle in a layer on the bottom, that part of the dish would become superheated and would be apt to break (see last paragraph in Note 6).

8. CRYSTALLIZATION

(*a*) A great number of pure substances are capable of assuming the crystalline condition when in the solid form.

Crystals are bounded by plane surfaces, which make definite and characteristic angles with each other and with the so-called axes of the crystals.

The external form of a crystal reflects in some manner the shape or structure of the individual molecules of the substance; for the crystal must be regarded as being built up by the deposition of layer on layer of molecules, all of which are placed in the same definite spatial relation to the neighboring molecules.

When a substance takes on the solid form very rapidly (as when melted glass or wax cools) its molecules do not have an opportunity to arrange themselves in a regular order, and consequently the solid body is *amorphous*. The axes of the individual molecules point in every direction without regularity, and consequently the solid body possesses no crystalline axes or planes.

It is evident from the above that the essential condition favoring the formation of perfect crystals is that the solid shall be built up very slowly. This is the only general rule which can be given in regard to the formation of perfect crystals.

The excellence of a chemical preparation is in many cases judged largely from its appearance. The more uniform and perfect the crystals, the better appearance the preparation presents.

In the following preparations sometimes a pure melted substance is allowed to crystallize by simply cooling; in such a case the cooling should take place slowly. More often crystals are formed by the separation of a dissolved substance from a saturated solution. Perfect crystals can best be obtained in this case by keeping the solution at a constant temperature and allowing it to evaporate very slowly. This is easily accomplished in industrial works where large vats of solution can be kept at a uniform tem-

perature with steam coils and allowed to evaporate day and night. On the laboratory scale it is almost impossible, first on account of variations in temperature, and next on account of dust which must fall into an uncovered dish.

The majority of substances are more soluble at higher temperatures than at lower. If a solution just saturated at a high temperature is allowed to cool very slowly, it is possible for the solid to separate so slowly as to build up perfect crystals. This is an expedient that can be adopted to advantage in several of the following preparations. In many cases, however, when a saturated solution cools it becomes *supersaturated*, sometimes to a high degree. Then when crystallization is once induced it occurs with such rapidity that a mass of minute crystals, instead of a few large, perfect ones, is produced. To avoid this supersaturation a few *seed crystals* (*i. e.*, very small crystals of the kind desired) may be placed in the solution. These form nuclei on which large crystals can be built up, and when they are present it is impossible for the solution to remain supersaturated.

In carrying out the following preparations the principles just stated should be kept carefully in mind ; but in many instances specific suggestions will be given as to the easiest method for obtaining good crystals of any particular substance.

Large crystals, it is true, present a pleasing appearance, but oftentimes they contain a considerable quantity of the mother liquor inclosed between their crystal layers. Hence if purity of product is the sole requisite, it is often more desirable to obtain a *meal* of very fine crystals. Such a meal is obtained by crystallizing rapidly and stirring while crystallizing. Some substances are so difficult to obtain in large crystals that it is more satisfactory to try only to obtain a uniform crystal meal.

(*b*) *Purification by Recrystallization.* — When a given substance crystallizes from a solution, it most generally separates in a pure condition irrespective of any other dissolved substances the solution may contain. Thus a substance can be obtained in an approximate state of purity by a single crystallization. Portions of the mother liquor (containing dissolved impurities) are, however, usually entrapped between the layers of the single crystals, not to mention the liquid which adheres to the crystal surfaces. By dissolving the crystals, the small amount of impurity likewise passes into the solution, but only a small fraction of this impurity is later entrapped by the crystals when they separate from this new mother liquor. By several recrystallizations, then, a substance can ordinarily be obtained in a very high state of purity.

9. DRYING

(*a*) A preparation that is not affected by the atmosphere can be dried by being spread in a thin layer on a plate of glass, on filter paper, or, best of all, on an unglazed porous porcelain plate.[1] The substance may with advantage be turned over occasionally with a spatula; and if it is not decomposed by heat it can be dried more rapidly in a warm place, such as over the steam table. *A product containing water of crystallization should never be dried at an elevated temperature.* During the drying the preparation must, of course, be carefully protected from dust.

(*b*) *Substances which decompose on standing exposed to the air* may be quickly dried if they are first rinsed with alcohol, or with alcohol and then ether. Rinsing with alcohol removes nearly all of the adhering water, and a further rinsing

[1] Dishes which are imperfect, and on that account have not been glazed, can be obtained very cheaply from the factories.

with ether removes the alcohol. Alcohol evaporates more rapidly than water, but ether evaporates so rapidly that a preparation wet with it may be dried by a very few minutes' exposure to the air.

Alcohol and ether are both expensive and should be used sparingly. They can be used most effectively as follows: After all the water possible has been drained from the preparation, transfer the latter to an evaporating dish and pour over it enough alcohol to thoroughly moisten it; stir it with a spatula until the alcohol has penetrated to every space between the crystal grains, then pour off, or drain off, the alcohol and treat the preparation in like manner with another portion of fresh alcohol. After that wash it once or twice with ether in exactly the same manner. If it is necessary to wash the preparation on the filter, drain off the water as thoroughly as possible, stop the suction, add just enough alcohol to moisten the whole mass, and after letting it stand a few moments drain off the liquid completely. Apply a second portion of alcohol and portions of ether in the same manner.

10. PULVERIZING

In chemical reactions in which solid substances are involved the action is limited to the surface of the solid, and for this reason it is evident that it must be much slower than reactions which take place between dissolved substances; it is also evident that the more finely powdered a solid substance, the greater is its surface, and therefore the more rapidly it will react.

Most solid raw materials for the following preparations are supplied in the powdered form, but they are rarely powdered finely enough; they should in general be further pulverized until they no longer feel gritty beneath the pestle or between the fingers.

For grinding any quantity of a substance a large porcelain mortar (say 8 inches in diameter) with a heavy pestle is preferable to the small mortars usually supplied in the desks.   One or more such mortars is placed in the laboratory for general use.

If a hard substance can be obtained only in large pieces, it should first be broken with a hammer, then crushed into small particles in an iron or steel mortar, after which it is to be ground in the porcelain mortar.   In the final grinding it is often advisable to sift the fairly fine from the coarser particles, then to finish grinding the former by itself and to crush and grind the coarser particles apart.

DRY REACTIONS: FURNACES

Dry solid substances do not react appreciably with each other at ordinary temperature.   Reactions are made possible in two ways: first, the *wet way*, in which the substances are dissolved and thus brought into most intimate contact. In many cases solution also produces ionization, which, as is known, greatly increases chemical activity.

Reactions in the *dry way* are rendered possible by heat. Heat alone increases the rapidity of a chemical reaction, it being a general law that the speed is increased from two to three times for every increase of $10°$ C. in temperature. In cases in which one or more of the reacting substances are melted by the heat, the same sort of intimate contact is brought about as in the case of solutions.   Fusion is likewise a means of producing electrolytic dissociation, and on this account also it increases chemical activity.

In some of the furnace reactions in which none of the substances are melted, as, for example, in the reduction of strontium sulphate to strontium sulphide by means of charcoal (see Preparation No. 6), the process probably takes

place in virtue of a certain amount of gas which is continuously regenerated. A little of the hot charcoal is oxidized to carbon monoxide, which then reduces some of the strontium sulphate, it being itself changed to carbon dioxide thereby; the latter gas comes in contact with incandescent charcoal, and carbon monoxide is again produced.

Reactions in the *dry way* are usually carried out in crucibles — of iron, clay, or graphite, according as to which is least attacked by the reagents. For rather moderate temperatures the crucible may be heated over a flame, but in most cases the requisite temperature can best be obtained in a furnace.

The form of furnace most to be recommended for this work is represented in Figure 5. It consists of a cylinder of fire clay, 7 inches high

FIG. 5

and 6½ inches in external diameter, which is surrounded by a sheet iron casing. It is heated, as shown, by a gas-wind flame, introduced through an opening in the lower part of one side. If a suitable air blast is not available, a gasoline blowpipe (such as is commonly used by plumbers) is almost equally serviceable.

When such a furnace as that described is heated as hot as possible with a well-regulated mixture of gas and air, a temperature of about 1,350° can be obtained. For carrying out ordinary chemical preparation work an accurate enough measure of the temperature is given by the color of the glowing interior of the furnace, and the approximate cen-

tigrade values corresponding to different colors are as
follows :
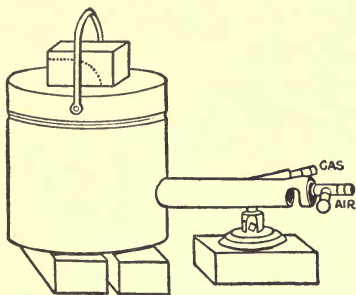
Incipient red heat	$550°$
Dull red heat	$650°$
Red heat	$800°$
Bright red heat	$1,000°$
Yellow heat	$1,200°$
White heat	$1,350°$

CHAPTER I

ALKALI AND ALKALINE EARTH METALS

These metals constitute the left hand or A families in the first two groups of the periodic classification of the elements, as shown in the table which appears in the appendix, and which is also placed for convenience inside the front cover of the book.

The metals of these two families are studied together because they are the extremely active base-forming elements. On account of their great activity they are never found uncombined in nature, and it is only by the aid of the most powerful reducing agencies (for example, by electrolysis of their molten salts) that the metals themselves are extracted from their compounds.

The alkali metals are monovalent. Their hydroxides, MOH, are extremely soluble and are highly dissociated as bases; on account of the corrosive properties of the latter they are known as the caustic alkalies — hence the designation, *alkali metals*. The compounds of the alkali metals are, with a very few exceptions, soluble in water, and they are all strong electrolytes.

The radical ammonium, NH_4, is classed with the alkali metals on account of its ability to form the same kinds of compounds.

The alkaline earth metals are divalent; their hydroxides, $M(OH)_2$, are less soluble than those of the alkali metals, but are nevertheless very strongly basic. The compounds of these metals are not so generally soluble as those of the alkali metals, and in particular the carbonates and sulphates are mostly insoluble.
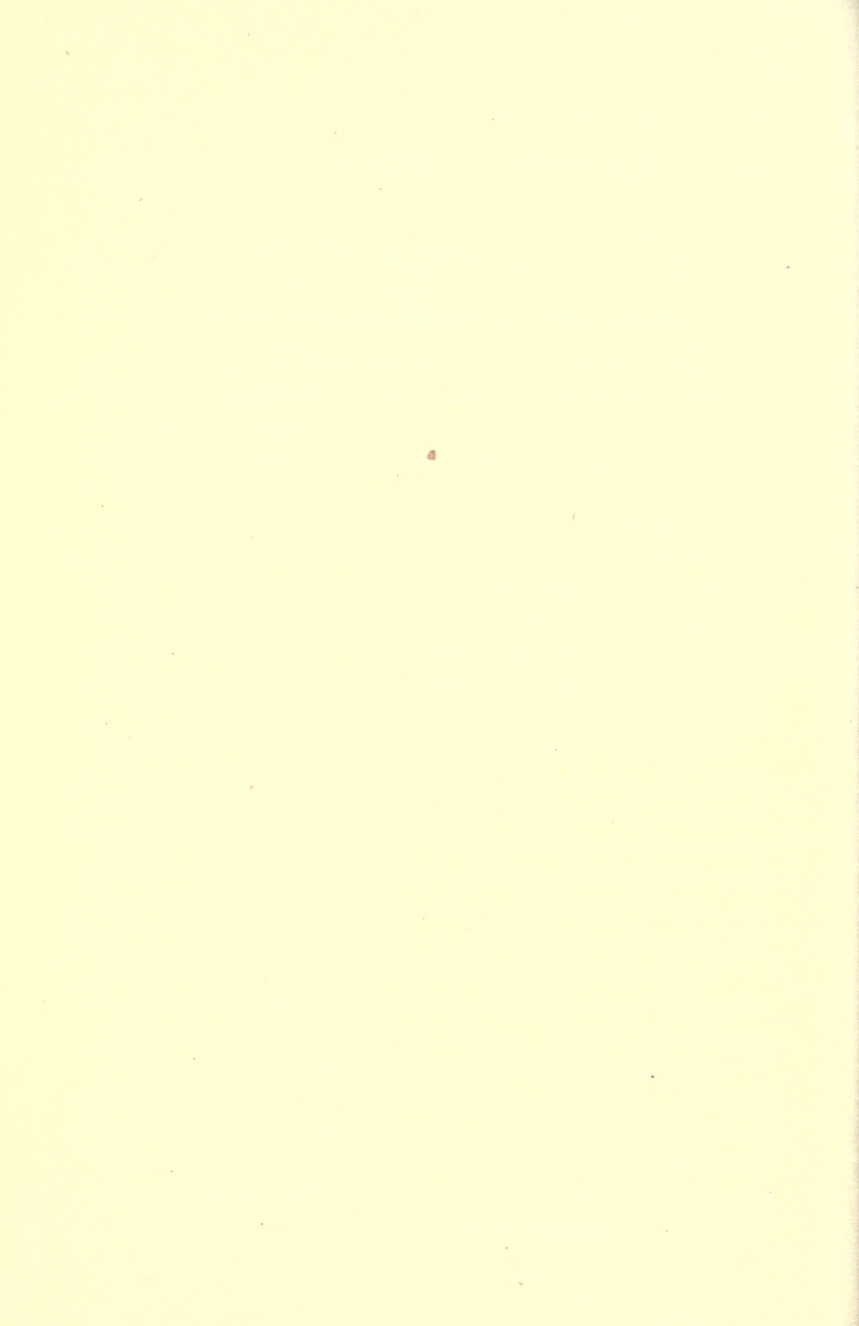
I. POTASSIUM NITRATE FROM SODIUM NITRATE AND POTASSIUM CHLORIDE

The most important source of nitrates is Chili saltpeter, sodium nitrate. This is not suited for use in explosives on account of its property of attracting moisture and rendering the explosive preparation damp. Potassium nitrate is not open to this objection, and hence large quantities of it are prepared, using sodium nitrate as a source of the nitrate radical.

When two ionizable salts are dissolved in water the resulting solution will contain, besides the undissociated molecules and the ions of these two salts, also the undissociated molecules of the two new salts which form by the interaction of the ions present. Which of these four salts will crystallize first out of solution depends upon their relative solubility. Thus if sodium nitrate and potassium chloride are dissolved together in water the resulting solution will contain Na^+, K^+, NO_3^-, and Cl^--ions, together with undissociated molecules of $NaNO_3$, $NaCl$, KNO_3, KCl. The solubility of some salts varies very much with the temperature, while that of other salts varies very little. This is seen from the following table and diagram, and practical use is made of these facts by crystallizing successively the two different salts at different temperatures.

GRAMS OF SALT SOLUBLE IN 100 GRAMS OF WATER

	At 10°	At 100°
KNO_3	21	246
NaCl	36	40
KCl	31	56
$NaNO_3$	81	180
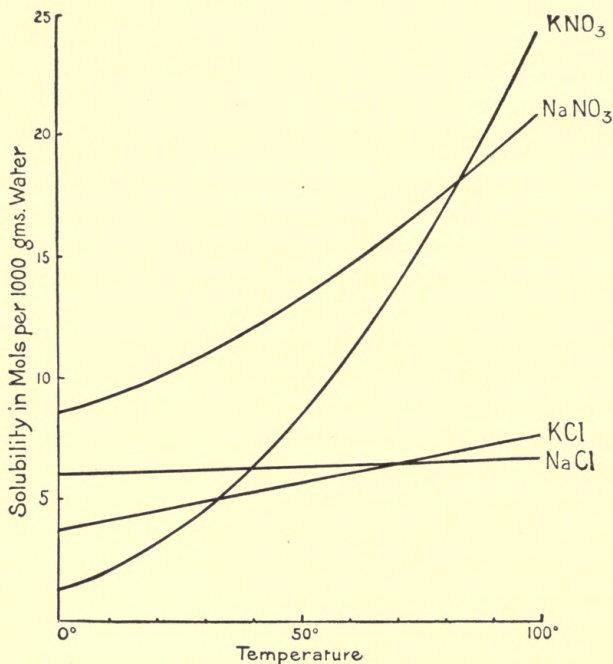
Procedure. — Dissolve 100 grams of sodium nitrate and 88 grams of potassium chloride in 200 cc. of water and evaporate in a porcelain dish to half that volume. Without letting the liquor cool, separate it from the crystals which have formed during the evaporation. This is best accomplished with the aid of suction (see Note 4 (*b*) on page 7, Witt filter). The liquid is poured through the filter and then the crystals are thrown upon the plate and pressed with a spatula, while applying gentle suction in order to remove as much as possible of the liquid clinging to them. Pour the filtrate into a beaker and set it aside to cool; then examine the crystals left on the filter and convince yourself

that they consist in the main of sodium chloride. (Examine with a microscope. The crystals should be cubical. Compare the taste with that of pure sodium chloride and that of pure potassium nitrate.) By means of running tap water cool the filtrate to about 10°, and then separate the crystals of potassium nitrate from the liquid in the same manner as above (see Note 3 on page 7, last sentence). The filtrate from these crystals is saturated with both sodium chloride and potassium nitrate, and the larger part of the latter should be saved. Evaporate the solution in a smaller dish until a considerable quantity of sodium chloride crystallizes from the boiling liquid. Filter hot, as above, and crystallize potassium nitrate from the filtrate by cooling. Unite this crop of potassium nitrate crystals with the first. Test a very small portion of them for sodium chloride by dissolving about 0.1 gram in 2 cc. of water and adding a drop of silver nitrate solution. They are not pure and must be purified. Weigh roughly the crystals while still moist, and dissolve them in from half to three-quarters of their weight of hot water. Cool and separate the crystals from the mother liquor. The latter should now contain nearly all of the sodium chloride which was mixed with the first crop of crystals. Test as above to see if this crop is free from sodium chloride. If not, repeat the recrystallization as many times as is necessary to get a perfectly pure product. A little of this should when dissolved give no turbidity with silver nitrate solution, and when held in the flame on a platinum wire should color it the violet color of potassium, with none of the yellow sodium color. Spread the preparation on an unglazed porcelain plate and allow it to dry by standing exposed to the air; then put up the salt in a test tube or a small bottle, and label it neatly.

Questions

1. Define metathesis.

2. When a metathetical reaction is carried out in the *wet way*, why is the solubility of the substances involved of importance? Explain why, according to this point of view, the reactions $AgNO_3 + KCl = AgCl + KNO_3$ and $BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$ are much more complete than the reaction $NaNO_3 + KCl = KNO_3 + NaCl$.

3. Explain why fewer operations should be required to prepare potassium nitrate from potassium sulphate and barium nitrate than by the foregoing procedure.

2. CAUSTIC POTASH FROM WOOD ASHES

Of the mineral constituents of plants, potassium salts form an important part, and, so far as these are salts of organic acids, they are converted into potassium carbonate when the plant is burned. On an average, wood ashes contain about 10 per cent. of potassium carbonate, and before the advent of the Leblanc Soda Process this was almost the sole supply of alkali. Even after this process came into general use, by which sodium carbonate could be obtained from common salt, wood ashes remained for some time the important source of potassium carbonate. In recent years, however, the greater part of the production of potassium carbonate has been derived by the Leblanc Process from potassium salts found in deposits in the earth, principally at Stassfurt, Germany.

Potassium carbonate being the principal soluble constituent of wood ashes, it is extracted with water; but the extract so obtained contains, as well, the other soluble mineral constituents, and also a considerable amount of tarry coloring matter which was not destroyed in the combustion of the wood. This tarry matter is destroyed by calcination of the residue obtained on evaporating the aqueous extract, and the calcined mass is what is known

as crude potash. A better grade of commercial potash can be obtained by dissolving this mass in water, filtering, and evaporating the solution.

In order to obtain potassium hydroxide or *caustic potash* from potassium carbonate the solution of the latter is treated with milk of lime (calcium hydroxide). With this it interacts, yielding insoluble calcium carbonate and soluble potassium hydroxide,

$$Ca(OH)_2 + K_2CO_3 = CaCO_3 + 2KOH.$$
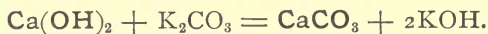
Procedure. — Tie a piece of cloth over the mouth of a thistle tube and insert it beneath the surface of a layer of sand, one-half inch deep, in the bottom of a tall 2-liter bottle. Mix 1 kilogram of wood ashes with 800 cc. of hot water in a pail, and transfer the moist mass to the bottle. Pour 200 cc. more of hot water over the surface of the ashes. Connect the thistle tube with a siphon and draw off as much liquid as possible, perhaps 200 cc., using suction and drawing the liquid into a suction bottle if it does not otherwise run rapidly enough. Commence evaporating this liquid in an 8-inch evaporating dish; then pour 300 cc. of hot water on top of the ashes and stir around the surface layer. Again draw off about 300 cc. of liquid and add it to that in the evaporating dish, and repeat the operation until the liquid drawn off is nearly colorless. Not more than 2 to $2\frac{1}{2}$ liters need be drawn off in all. When the liquid is all evaporated remove the dry residue to an iron dish and heat it strongly with a Bunsen burner to destroy the tarry matter. More than a moderate red heat should not be exceeded, as it is not desirable to fuse the salt, but the heating should be continued until the ash is white or at most contains only black specks of completely charred carbon. When cooled, weigh the material; assuming it to consist wholly of potassium carbonate, calculate

the amount of quicklime (calcium oxide) necessary to react with it according to the equation,

$$CaO + H_2O + K_2CO_3 = 2KOH + CaCO_3.$$
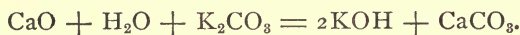
Slake 20 per cent. more than that amount of lime by covering it in a porcelain dish with water and quickly pouring off the excess of water. If the lime is of suitable quality it will soon grow hot and crumble to a powder, $Ca(OH)_2$. Take sufficient water to make ten times the weight of the crude potash. Stir up the slaked lime with half of it, thus making milk of lime. Dissolve the potash in the other half, bring it to boiling, and add the milk of lime with stirring. Let the mixture boil for 15 minutes and then filter, using a suction bottle (see Note 4 (*b*), Witt filter). Measure the volume of the solution of caustic potash obtained and preserve it in a stoppered bottle.

Test the strength of the solution. Measure 15 cc. with a pipette into a beaker and add a drop of litmus solution. Run into this from a burette a solution of *normal* hydrochloric acid (36.5 grams per liter), drop by drop, until the color just changes from blue to red. If the right point is overstepped begin again with a fresh sample of the solution. From the amount of acid taken to neutralize the sample, calculate the amount of KOH obtained from the wood ashes. Preserve the solution in a bottle labeled with the number of cubic centimeters of the solution, with its strength in mols per liter of potassium hydroxide, and with the actual amount in grams of the potassium hydroxide.

Questions

1. The calcium hydroxide used in causticizing the potash is a slightly soluble solid suspended in water, its solubility being 1.7 grams per liter. Explain how, in spite of its limited solubility, the required amount can enter into reaction.

2. Explain why the caustic potash solution obtained contains practically no calcium ions, even in case an excess of calcium hydroxide may have been used for causticizing.

3. Analyses of the crude potash obtained from various grades of wood ashes have given results which fall within the limits given in the table:

K_2CO_3	.	.	.	38–78 per cent.
Na_2CO_3	.	.	.	0–12 per cent.
K_2SO_4	.	.	.	13.5–40.5 per cent.
KCl	.	.	.	0.9–10.0 per cent.
Insoluble matter		.	0.1–9.2 per cent.

What substances other than KOH would you expect then to be present in the caustic potash solution which you have prepared? Look up the solubility of calcium sulphate and calcium hydroxide, and decide whether, in the presence of a large amount of potassium hydroxide, milk of lime would react with a small amount of potassium sulphate according to the equation:

$$K_2SO_4 + Ca(OH)_2 = CaSO_4 + 2KOH.$$
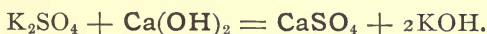
4. If a solid substance crystallizes from the caustic potash solution after it has stood, decide what it is by consulting the table in Question 3 and a solubility table.

3. SODIUM CARBONATE BY THE AMMONIA PROCESS

The principle employed in the manufacture of sodium carbonate from sodium chloride by the Solvay Process is exceedingly simple. It depends primarily upon the fact that sodium acid carbonate is but sparingly soluble in water; this compound is produced by the interaction of so-

dium chloride, in a saturated salt solution, with ammonium acid carbonate,

$$(1) \quad NaCl + NH_4HCO_3 \rightleftharpoons \mathbf{NaHCO_3} + NH_4Cl.$$
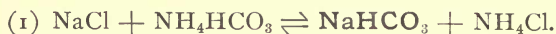
Since ammonia and salts of ammonium are very much more expensive than sodium carbonate, it is evident that the process can be of no commercial value unless ammonia can be recovered and used again. This is accomplished in fact by treating the mother liquor, after separation from the sodium bicarbonate, with calcium hydroxide,

$$(2) \quad Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O.$$

In practice the process is usually carried out as follows:

A nearly saturated salt solution is purified of iron, magnesia, lime, etc., which would otherwise get into the final product; there is then passed into it ammonia gas until it has absorbed 60 to 70 grams of NH_3 per liter, whereupon carbon dioxide is passed in until it has reacted with the ammonia to form ammonium bicarbonate,

$$NH_4OH + CO_2 = NH_4HCO_3,$$
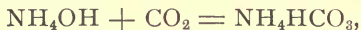
which in turn reacts with the salt according to (1). Extensive precautions necessarily have to be observed that practically no ammonia escape during the process, so that the entire amount may be used over and over again. It is also essential that as little carbon dioxide shall be wasted as possible. Thus the carbon dioxide is utilized which is produced in converting limestone into quicklime,

$$CaCO_3 \rightarrow CaO + CO_2,$$
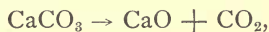
and in converting sodium bicarbonate into sodium carbonate,

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

Procedure. — To 50 cc. of concentrated ammonium hydroxide (sp. gr. 0.90) add 150 cc. of water. Place in a flask

and add 60 grams of table salt free from lumps.   Shake until the salt is nearly or quite dissolved and filter the solution if it is not perfectly clear.   Pass a delivery tube through one hole of a double-bored, tightly fitting stopper placed in a 300 cc. flask.   Provide a plug for the other hole. Let the tube dip into the solution which is placed in the flask, and pass in carbon dioxide gas from a Kipp generator until all the air has been displaced from the flask; then close the flask and allow the gas to pass in as fast as it will be absorbed.   Occasionally, as the action seems to slacken, loosen the plug for a moment.   Shake the flask frequently.   It will take several hours for the solution to absorb sufficient carbon dioxide, and it may be left over night connected with the generator.   When no more gas can be absorbed pour the mixture from the flask upon a Witt filter (see Note 4 (*b*)).   Apply suction to remove the liquid from the sodium bicarbonate.   Wash the product three times with 15 cc. of ice water (see Note 5 (*a*), on page 12), sucking it free from liquid each time.   Spread the preparation on an unglazed plate and leave it until it ceases to smell of ammonia.   Test the preparation for chlorides (see Question 1), of which it should not contain more than a trace.

Questions

1. In testing the preparation for chlorides, the test solution must be acidified with nitric acid before silver nitrate is added.   What other silver salt would otherwise be precipitated?   How does the presence of nitric acid prevent this?

2. How is sodium carbonate prepared from sodium bicarbonate?

3. What is an acid salt?   How does a solution of an acid salt such as $KHSO_4$ behave towards litmus?   Test the

behavior of solutions of $NaHCO_3$ and of Na_2CO_3 towards litmus.   Explain the cause of this behavior.

4.   Why cannot potassium carbonate be prepared from potassium chloride by the ammonia process?   (Look up the solubility of potassium bicarbonate.)   What process may be used to obtain potassium carbonate from this source?

4.   CHEMICALLY PURE SODIUM CHLORIDE FROM ROCK SALT

Common rock salt may contain other than sodium chloride up to 10 per cent. of matter, which consists in the main of the sulphates and chlorides of potassium, calcium, and magnesium, not to mention a considerable amount of dirt and insoluble matter.   For most commercial purposes these impurities are not harmful.   By careful crystallization of the salt from solution, a product sufficiently free from these impurities can be obtained to be used as table salt. To obtain *chemically pure* sodium chloride, however, more elaborate precautions must be taken.   A satisfactory method depends upon the insolubility of sodium chloride in a concentrated solution of hydrochloric acid.   A nearly saturated solution of the rock salt is prepared, and, without removing the dirt and insoluble matter, enough pure sodium carbonate is added to precipitate the calcium and magnesium in the solution as carbonates.   Into the clear filtrate is then passed gaseous hydrochloric acid until the greater part of the sodium chloride is precipitated, while the small amounts of sulphates and of potassium salts remain in the solution. The precipitate is drained and washed with a solution of hydrochloric acid until the liquid clinging to the crystals is entirely free from sulphates.

Procedure. — Dissolve 25 grams of rock salt in 75 cc. of water, hastening the action with gentle heating.   To the

solution add about 1 gram of sodium carbonate dissolved in a few cubic centimeters of water. Stir, let settle, and add a few drops more of sodium carbonate solution, and if no fresh precipitate is produced in the clear part of the
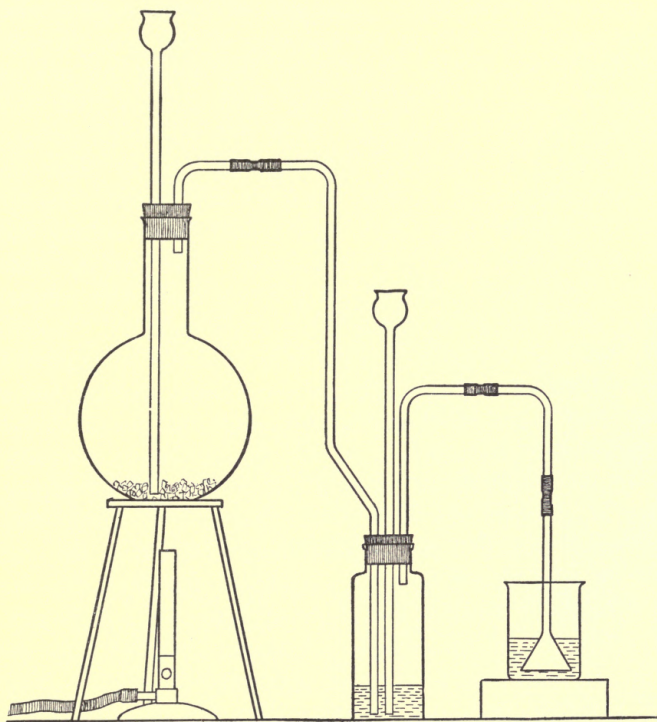
FIG. 6

solution no more need be added; otherwise enough more must be added to produce this result. Filter the solution, hot, through an ordinary filter (Note 4 (c)). Prepare pure gaseous hydrochloric acid as follows: Place 50 grams of dry rock

salt in a round-bottom liter flask provided with a rubber
stopper with two holes, through which pass a thistle tube
reaching to the bottom of the flask, and an exit tube just
coming through the stopper. Provide a wash bottle for
the gas as follows: A 300 cc. bottle is provided with a
stopper with three holes. Through one passes a glass tube
reaching to the bottom for entrance of the gas; through
another a thistle tube reaching to the bottom for use as
a safety tube; and through the third an exit tube just
coming through the stopper. Pour into the bottle enough
concentrated hydrochloric acid (sp. gr. 1.2) to come up
three-quarters of an inch on the two lower tubes. Connect
the exit tube with a 2-inch filter funnel for delivering the
gas into the sodium chloride solution. Use entirely glass
tubing, and, where connections must be made with rubber,
bring the ends of the glass tubes close together. Before
commencing to use this apparatus it must be approved
by an instructor. Pour the sodium chloride solution into a
beaker of 3 inches diameter, and insert the mouth of the
funnel below the surface of the liquid. Pour gradually
95 cc. of concentrated sulphuric acid into the generating
flask, and when the first action has ceased warm very
gently. There will be a great deal of frothing, but the
froth should at no time be allowed to get over into the
wash bottle.[1] When hydrochloric acid gas ceases to be gen-
erated, separate the precipitated sodium chloride from the
mother liquor by pouring it upon a Witt filter. Suck
the moisture from the crystals. Test the filtrate for sul-
phate by adding a little barium chloride solution to a
small sample of it diluted with water. A strong test will
probably be obtained. Now wash the crystals with succes-

[1] The melted sodium acid sulphate left in the generating flask is
very hot and must not be poured into the sink. It may be poured into
some *dry* receptacle specially provided, or it may be allowed to cool
slowly and solidify in the flask and then be dissolved out with water.

sive portions of 10 cc. of hydrochloric acid solution of 1.12 sp. gr. until the washings show no further test for sulphates. (See Note 5 (*a*).)   Then transfer the crystals to a porcelain dish and heat gently, while stirring, until all decrepitation ceases.

Questions

1.   Why must the hydrochloric acid gas be passed through a washing bottle?   Why is the safety tube necessary?

2.   Why, in the light of the Mass Law, should one expect the solubility of sodium chloride to be lessened by the presence of hydrochloric acid?   [It may be stated that another effect also comes into play here which likewise tends to lessen the solubility of sodium chloride.]

3.   Mention two possible causes for the very considerable amount of heat produced when the hydrochloric acid gas is absorbed by the solution in the beaker.

5.   AMMONIUM BROMIDE

Ammonium bromide could be prepared by the neutralization of ammonium hydroxide with hydrobromic acid,

$$NH_4OH + HBr = NH_4Br + H_2O.$$
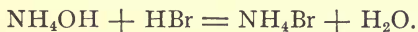
Since, however, hydrobromic acid is a more expensive material than uncombined bromine, the latter would have the preference as a source of bromine, provided it yielded as satisfactory a product.   Chlorine or bromine reacts as follows upon a cold solution of *sodium* hydroxide, as, for example, in the manufacture of bleaching liquors,

$$Br_2 + 2NaOH = NaBr + NaBrO + H_2O,$$
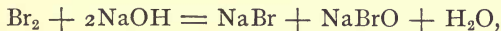
with the formation of sodium hypochlorite or hypobromite. Sodium hypobromite reacts with *ammonium* hydroxide according to the equation,

$$3NaBrO + 2NH_4OH = 3NaBr + 5H_2O + N_2.$$
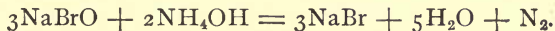
Thus the action of bromine upon ammonium hydroxide yields only ammonium bromide and nitrogen gas, because even if the primary effect were to yield bromide and hypobromite in equal quantities, as is the case if sodium hydroxide is used, the ammonium hypobromite would immediately react with fresh ammonia in the same manner as does sodium hypobromite.

Procedure. — Place 55 cc. of concentrated ammonia (sp. gr. 0.90), together with 50 cc. of water, in a flask, which should be set in a pan of ice water. Put 15.8 cc. of bromine in a small separatory funnel,[1] and add it a drop at a time to the ammonia, rotating the flask after each drop until the yellow color produced by the bromine has completely disappeared. Do not allow the contents of the flask to become heated at any time, as a dangerously explosive compound might in that case be formed. As soon as a permanent yellow color is produced, stop adding bromine and add at once a few drops of ammonia until the solution has again become colorless. Place the solution in an evaporating dish on top of a beaker of boiling water, and let the salt crystallize as the water evaporates. When only a little liquid remains, separate the crystals from it in a funnel, and dry them on a porcelain plate.

Questions

1. What products would be formed if bromine were added to a solution of sodium hydroxide instead of ammonium hydroxide, (1) if the solution were kept cold? (2) if it were heated?

2. *Experiment.* — Add about 10 drops of bromine to

[1] The stopcock of the funnel should first be lubricated with vaseline or grease and then fastened with a rubber band. Bromine produces very bad burns when it gets upon the hands. To avoid danger of accident ask an instructor to approve the apparatus before beginning actual operations with the bromine.

10 cc. of a cold 10 per cent. sodium hydroxide solution. Add this gradually to a solution of ammonium hydroxide, made by diluting 1 cc. of desk reagent with 10 cc. of water. Determine what gas is given off.

3. Write the equation showing the complete reaction between bromine and ammonia. What fraction of the entire amount of ammonia used is lost through formation of nitrogen gas?

4. Why cannot hydrobromic acid be prepared from potassium bromide by a method analogous to that used in the manufacture of hydrochloric acid?

5. Explain why, from the standpoint of economy, the method of preparation above outlined is superior to the direct neutralization of ammonia with hydrobromic acid.

6. STRONTIUM HYDROXIDE FROM STRONTIUM SULPHATE

One of the most important sources of strontium is the mineral celestite, $SrSO_4$. By reduction with charcoal this can be converted into strontium sulphide,

$$SrSO_4 + 4C = SrS + 4CO,$$
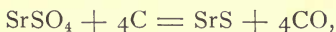
and the strontium sulphide by treatment with copper oxide and water can be made to yield strontium hydroxide,

$$SrS + CuO + H_2O = Sr(OH)_2 + CuS.$$
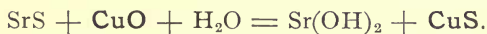
Copper oxide is in the ordinary sense insoluble; nevertheless in contact with water it does yield to an infinitesimal extent, first copper hydroxide, and then Cu^{++}-ions,

$$CuO + H_2O \rightleftharpoons Cu(OH)_2 \rightleftharpoons Cu^{++} + 2OH^-.$$

Therefore, since copper sulphide is a far more insoluble substance than copper oxide, it follows that the few

Cu^{++}-ions from the latter unite with the S^{--}-ions from the strontium sulphide to form copper sulphide, which precipitates continuously, while the copper oxide continuously goes into solution to resupply Cu^{++}-ions, and this action continues until either the copper oxide or the strontium sulphide is exhausted.

Strontium hydroxide crystallizes with 8 molecules of water, $Sr(OH)_2.8H_2O$. It is very soluble in hot water, but sparingly soluble in cold water.

Procedure. — Grind 50 grams of powdered celestite in a porcelain mortar until no more grit is felt under the pestle. Add 20 grams of powdered charcoal and continue to grind with the pestle until the two are thoroughly mixed. Place the mixture in a clay crucible, pack it firmly, and cover it with a layer of powdered charcoal $\frac{1}{2}$ inch deep. Cover the crucible with a close-fitting cover and heat it in a gas furnace for one hour, at a bright red heat (Instructions as to regulating the flame). After the contents of the crucible have cooled, remove the layer of charcoal from the surface and bring the remainder, after crushing it to a powder, into an 8-inch porcelain dish; add 300 cc. of water, bring the mixture to a boil, and while it is boiling add copper oxide, a little at a time, until all of the soluble sulphide has interacted with it, — about 40 grams in all. So long as any unchanged strontium sulphide is present the solution will show a yellow color, which may be observed by letting the black solid settle for a moment, and then looking through the upper layers of the clear liquid at the background of the white porcelain dish. As soon as the yellow color has entirely disappeared, the strontium sulphide has all reacted. Crystals of strontium hydroxide separate rapidly from this solution when it cools. Hence it must be filtered quickly in order to avoid having the crystals form in the filter and clog it completely. Heat 50 cc. of

water to boiling in a beaker, and keep it at this temperature until it is .required.   Add hot water to the dish to replace any lost by evaporation, and pour (Note 2) the hot solution through a Witt filter (Note 4 (*b*)), allowing the main part of the residue to remain in the dish.   Add the 50 cc. of hot water to this residue, stir it thoroughly, heating it for a moment over the flame, and then pour solution and residue into the filter and drain out all of the liquid.   Transfer the solution to an Erlenmeyer flask (or let it remain in the filter bottle), stopper the flask to exclude the air, and wrap it with a towel, so that the solution·may cool slowly and larger crystals may be formed.   Finally, after several hours cool the solution with running tap water and then collect the crystals on a Witt filter.   Drain the crystals for a moment, but do not draw too much air through them, as they retain all the carbon dioxide it contains.   Spread the moist product on filter paper, and allow it to dry as quickly as possible by contact with the air.   Stopper it in a sample bottle or tube as soon as it is dry.

Questions

1.   What constituent of the atmosphere must be excluded from the solution while crystallizing and as much as possible from the crystals while drying?   How would it contaminate the preparation?

2.   A sample of the preparation should dissolve nearly clear in hot water.   What will surely cause a slight cloudiness?

3.   How could strontium chloride be prepared from strontium sulphide?

4.   Give some other method by which strontium hydroxide could be obtained from strontium sulphide without the use of copper oxide.

5.   Starting with the mineral strontium carbonate, how

might strontium hydroxide be prepared ?   Strontium oxide ?
Strontium chloride ?

7. STRONTIUM CHLORIDE FROM STRONTIUM
SULPHATE

Strontium chloride might be prepared by treating
strontium sulphide, the intermediate product in the last
preparation, with hydrochloric acid. For the sake of illus-
trating another method, however, a process which does not
require the use of a furnace is here employed for decom-
posing the strontium sulphate.

The method consists in first converting the sulphate
into the carbonate by boiling it with a concentrated solution
of sodium carbonate, and then of dissolving the carbonate
in hydrochloric acid, thereby yielding a solution of the
chloride.   The conversion of solid strontium sulphate into
solid strontium carbonate furnishes an interesting illustration
of the principle of mass action, for the solubility of these
two salts in *pure water* is as follows :

	Solubility in grams per liter	Solubility in mols per liter
$SrSO_4$	0.011	0.0006
$SrCO_3$	0.0011	0.00007

Strontium sulphate would dissolve in the solution of sodium
carbonate in the same manner as it would in pure water
until it had saturated the solution and its solubility product,
which is equal to 0.0006×0.0006, was reached, but for
the fact that long before this could occur the solution
would be supersaturated with respect to strontium carbon-
ate, whose solubility product is only equal to $0.00007 \times$
0.00007.   Thus strontium carbonate is precipitated con-
tinuously as strontium sulphate dissolves ; and since the

solution cannot become saturated with the latter so long as there is a large excess of carbonate ions present, the solid salt finally remaining will consist entirely of strontium carbonate, provided a sufficient amount of sodium carbonate were employed. The reaction which takes place is, however, reversible,

$$\mathbf{SrSO_4 + Na_2CO_3 \rightleftharpoons SrCO_3 + Na_2SO_4,}$$
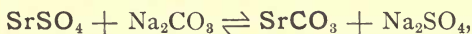
and, if strontium carbonate were boiled with a solution of sodium sulphate, the solid would be converted into the sulphate. It is easy to deduce that if the ratio of the concentration of the ions in solution $\dfrac{\text{conc } CO_3^{--}}{\text{conc } SO_4^{--}}$ is greater than $\frac{1}{74}$, solid strontium sulphate will be converted into solid carbonate.

Procedure. — Take 50 grams of powdered celestite. Grind it in a mortar until it is so fine that it no longer feels gritty under the pestle. Cover it in an 8-inch dish with 300 cc. of water, add 60 grams of anhydrous sodium carbonate, and boil the mixture for 30 minutes, stirring it constantly at first. Transfer the solution and solid to a tall, narrow beaker, using 100 cc. of fresh water in rinsing out the last of the residue, and let the solid matter settle for 5 minutes. Decant off the liquid, which is still somewhat cloudy, but from which the essential part of the solid has settled, and wash the residue three times by decantation with 400–500 cc. of water (see Note 5 (*b*), first paragraph). The residue is now sufficiently free from soluble sodium sulphate. Transfer about $\frac{1}{10}$ of the moist strontium carbonate to another beaker, to be used in a later part of the process. To the remaining $\frac{9}{10}$ add 50 cc. of hot water, and then add hydrochloric acid, drop by drop, while keeping the mixture at the boiling temperature, until the further addition of a drop of acid produces no more effervescence.

This solution now contains a slight excess of acid, which is to be neutralized by adding the remaining $\frac{1}{10}$ of the strontium carbonate. Add this,[1] and boil the mixture for 5 minutes. The solution should now be perfectly neutral to litmus. If it is acid, it shows that the hydrochloric acid was added carelessly and that there was thus more than could be neutralized by the strontium carbonate. Filter the perfectly neutral solution, and evaporate the filtrate until a faint scum forms on removing the solution from the flame and blowing vigorously across the surface. Allow the solution to cool, but stir occasionally in order to obtain a uniform crystal meal rather than a cake of crystals. Finally, drain the crystals on a Witt filter (Note 4 (*b*); evaporate the mother liquor to crystallization exactly as at first, and if the second crop of crystals is pure white, add it to the first crop. Dry the crystals of $SrCl_2.6H_2O$ by spreading them on an unglazed plate and exposing them to the air at room temperature. As soon as they are dried sufficiently so as not to cling together, bottle them at once, because they are somewhat efflorescent.

Questions

1. Explain why strontium carbonate, which is less soluble in pure water than strontium sulphate, should dissolve readily in dilute acids, while the latter salt will dissolve scarcely any more in acids than in pure water.

2. If a small quantity of a solution of strontium chloride were added to a solution containing equi-molal quantities of sodium carbonate and sodium sulphate, what would be the precipitate formed?

[1] If any iron salt is present, it should be oxidized by adding a few drops of chlorine water and boiling a moment before adding the strontium carbonate. The reason for such a procedure will be made clear later under Preparation 38, Manganous Chloride.

8. BARIUM OXIDE AND BARIUM HYDROXIDE
FROM BARIUM CARBONATE

The commercial method of preparing calcium oxide (quicklime) consists in heating calcium carbonate (limestone) in lime kilns. Barium oxide might be made from barium carbonate according to the same principle, except for the fact that the temperature required for the decomposition of barium carbonate is so high as to make such a method almost impracticable. This greater stability of the barium salt is an illustration of the fact that barium oxide is even more strongly basic than calcium oxide. The reaction, $BaCO_3 \rightleftharpoons BaO + CO_2$, is to some extent a reversible reaction, and in common with other reversible reactions it may be made to progress in one direction or the other by suitably altering the concentration of the substances present in the reacting mass. Of the three substances involved in this reaction the only one which can be removed during the course of the reaction is the carbon dioxide. It is, however, not enough to let it merely pass off as a gas, because there is already present in the atmosphere in the furnace enough carbon dioxide to force the reaction towards the left. The carbon dioxide must be chemically removed. This is accomplished by mixing powdered charcoal with the barium carbonate, for carbon reacts with carbon dioxide at a white heat and gives carbon monoxide. In the following procedure, in addition to the charcoal, a little rosin is mixed with the charge. On heating, the rosin decomposes and a deposit of soot is formed, which in this way becomes very intimately mixed with the charge.

The barium oxide obtained in this way is not pure, but contains particles of charcoal as well as impurities coming from the mineral. It is, however, very suitable for the manufacture of barium hydroxide, into which it is con-

verted by treatment with water. Barium hydroxide is extremely soluble in hot water, but sparingly so in cold water, from which it separates in flake-like crystals of the composition $Ba(OH)_2.8H_2O$.

Procedure. — Mix 100 grams of finely powdered barium carbonate (use either the mineral witherite or the artificially prepared barium carbonate) with 10 grams of powdered charcoal and 5 grams of rosin. After mixing the whole mass very thoroughly in a mortar, place it in a graphite crucible,[1] press it down firmly, and cover it with a layer of charcoal at least $\frac{1}{2}$ inch deep. Place a well-fitting cover on the crucible and heat the whole for one hour to as high a temperature as possible in the gas furnace. After the crucible has cooled, remove the top layer of charcoal, break up the mass of barium oxide, and add it rather cautiously to 400 cc. of water in a porcelain dish. (Note whether any heat is produced when barium oxide comes in contact with water.) Heat the mixture in the dish to boiling; pour the solution through a large, ordinary filter (Note 4 (*c*)), letting the clear liquid run directly into a 500 cc. flask. Rinse the residue in the dish with 75 cc. more of boiling water, and pour this upon the filter after the first portion has nearly all run through. Stopper the flask and allow the solution to cool slowly to room temperature; finally, cool it nearly or quite to 0°; collect the crystals on a Witt filter, and drain and dry them as directed for strontium hydroxide.

Questions

1. How does barium hydroxide become contaminated by exposure to the air? Why might this product be dried

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[1] If a clay crucible is used it should be lined with paper before putting in the charge. The paper chars and leaves a layer of carbon which separates the siliceous material of the crucible from the basic barium oxide and prevents their reacting to form a fusible compound .

with less contamination by exposure to the air out of doors than to the air of the laboratory?

2. The mineral witherite often contains barium sulphate as an impurity. State what changes this substance would undergo during the above process, and what resulting substance would be present to a small extent in the final crystallized product and to a greater extent in the mother liquor. (Compare preparation of strontium hydroxide from strontium sulphate.) Test both crystals and mother liquor for this substance. (How?) The final product can be quite satisfactorily purified from it by one or two recrystallizations. How might it be removed chemically? (See Strontium Hydroxide.)

3. Devise a method for preparing barium hydroxide from barium carbonate by which the use of a furnace may be avoided. *Suggestion.* — Make use of the difference in solubility of barium chloride and barium hydroxide.

GENERAL QUESTIONS. I

ALKALI AND ALKALINE EARTH METALS

Experiments

(The results observed are to be recorded in the laboratory notebook at the time the experiments are performed.)

1. Place a few small lumps of marble (pure calcium carbonate) in a small iron crucible, or a porcelain crucible lined with paper. Cover the crucible in order to keep in the heat, and heat it quite strongly for 20 minutes with a Bunsen flame. When the product has cooled, wet each lump with a single drop or two of water and wait a few minutes, if necessary, to observe the effect. Then wet the product with somewhat more water, and test the reaction of the moist mass towards litmus.

2. Burn a strip of magnesium ribbon, held with iron pincers, and let the ash fall in a porcelain dish. Wet the magnesium oxide with a single drop of water and place the moist mass on a strip of red litmus paper. Note the rapidity and intensity with which the litmus is turned blue.

3. To some magnesium chloride solution, add (*a*) some ammonium hydroxide; (*b*) some ammonium chloride and then some ammonium hydroxide. Observe in each case whether magnesium hydroxide is precipitated.

4. Dip a clean platinum wire in solutions of such of the chlorides of the alkali and alkaline earth metals as are at hand, and observe the color imparted to the Bunsen flame when the wire is inserted into the lower part of the flame.

Questions

1. What are the metals of the alkali group? Of the alkaline earth group? Give the symbols of the hydroxides and chlorides of the metals of each group. What is the characteristic valence of each group? With which group is the ammonium radical NH_4 classed?

2. Any oxy-salt, such as $CaCO_3$ ($= CaO.CO_2$), can be broken up by a sufficiently high heat into a basic oxide and an acid oxide — for example, $CaO.CO_2 \rightarrow CaO + CO_2$. The higher the temperature necessary to accomplish this, the greater is the chemical affinity between the two oxides, that is, the more strongly basic and acidic, respectively, are these two components; and therefore in a series of salts, all containing the same acidic oxide — for example, $CaCO_3$, $SrCO_3$, $BaCO_3$ — the greater the stability of the salt, the stronger is the basic oxide.

Look up in the text-books how easily the carbonates of sodium, potassium, calcium, and barium are decomposed by heat (compare Experiment 1 and Preparation 8); also to what extent and how readily the nitrates of the same metals are decomposed. From these data arrange the oxides of these four metals in the order of their strength as bases.

Which are more strongly basic, the oxides of the alkali or of the alkaline earth metals?

3. To what extent are the hydroxides of sodium, potassium, calcium, and barium dissociated electrolytically in aqueous solution? Does there seem to be any parallel between the basic strength of an oxide, as judged from the standard explained under Question 2, and the degree of dissociation of the base derived from it when the latter is dissolved in water?

4. Compare the solubility of calcium and magnesium hydroxides (Experiments 1 and 2). Explain the results observed in Experiment 3.

5. Tabulate the colors obtained by the flame tests for the alkali and alkaline earth metals (see Experiment 4 and text-books).

CHAPTER II

ELEMENTS OF THE THIRD GROUP OF THE PERIODIC SYSTEM

Boron and aluminum, the first two members of this group, are the only ones which are classed among the common elements. On this account, and also because the difference in properties between Family A and Family B is far less marked than in Groups I and II, the whole group is taken up under one heading.

The characteristics of this group are that the elements possess a valence of three, and that the oxides, M_2O_3, have but a weakly developed basic character. Boron, in fact, shows practically no base-forming properties, but forms rather the weak boric acid. The oxide of aluminum displays both basic and acidic properties; that is, it is *amphoteric.* The remaining elements are more distinctly base-forming than aluminum, without, however, approaching in any way the alkaline earth metals in this respect.

9. BORIC ACID

In this preparation, borax, the sodium salt of tetraboric acid, is chosen as the source of boron. Although boron is decidedly a non-metal, still its acid-forming characteristics are not highly developed. Its acids, therefore, having a low degree of ionization, are readily displaced by strong acids from solutions of their salts. Thus tetraboric acid would be set free from borax by hydrochloric acid; but since this is capable in aqueous solution of combining with water, and since normal boric acid (H_3BO_3) is but slightly soluble, it is this substance which crystallizes from the solution.

Procedure. — Dissolve 100 grams of borax in 300 cc. of boiling water. Add hydrochloric acid (about 41 cc. of conc. acid 1.2 sp. gr.) to the hot solution until a strip of blue litmus paper is colored bright red. Allow to cool, when normal boric acid will crystallize out. Filter off the crystals, using a Witt filter, and purify them by recrystallization, dissolving in 300 cc. of hot water. Allow to cool slowly, shaking or stirring occasionally to prevent the crystals from caking together.

Questions

1. Explain the relations between normal boric acid, metaboric acid, tetraboric acid, and boric anhydride. *Experiment.* — Place a few grams of boric acid on a watch glass upon the steam table (100–110°) and leave for ½ hour. What is formed? What would be formed if the acid were heated to 140°? Suspend a little of the acid in a loop of platinum wire, and heat in the Bunsen flame. What is formed?

2. *Experiment.* — Place a few grains of boric acid in a small porcelain dish, cover it with 5 cc. of alcohol, set fire

to it, and observe the color of the edges of the flame, especially when stirring and when the alcohol is almost burned out. Repeat, using borax instead of the boric acid, and again, using borax moistened with concentrated sulphuric acid.

What causes the green color of the flame, and why is it not observed with borax alone?

Repeat if necessary the last part of the preceding experiment, noticing the color imparted to the flame while the orthoboric acid is first melting, and again when a clear bead of boric anhydride is obtained.

What conclusions can you make from these experiments regarding the volatility of boric acid and of boric anhydride?

3.   What effect has a solution of borax upon litmus? Explain what is thus shown regarding the strength of boric or tetraboric acid.   Explain why litmus will not be turned a bright red until more than two molecules of HCl have been added to one molecule of borax.

4.   How can chloride of boron be prepared?   How does this substance behave when treated with water?   How would it behave if boron were a strongly metallic element?

10. ALUM FROM CRYOLITE

(BY–PRODUCT: SODIUM CARBONATE)

A characteristic series of compounds of the trivalent metals are the alums, of which the potassium aluminum, or common alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, is typical. These compounds are particularly interesting from the readiness with which they can be produced in large and beautiful crystals, and from the fact that any of the univalent alkali metals may take the place of potassium, or any one of a large number of the trivalent metals may take the place of aluminum in the common alum without altering the form or chemical nature of the crystals produced.

Of the many raw materials which might serve as the source of aluminum, cryolite, the double fluoride of sodium and aluminum, $3NaF.AlF_3$ or $Na_3(AlF_6)$, has been chosen, partly because it actually serves as an important source of aluminum compounds, and partly because its decomposition illustrates important chemical reactions and manipulations.

This mineral, although itself insoluble in water, will, if boiled with a suspension of milk of lime $(Ca(OH)_2)$, undergo a metathesis, with the formation of insoluble calcium fluoride, and a soluble salt of aluminum, in which this metal plays the part of an acid-forming element,

$$3NaF.AlF_3 + 3Ca(OH)_2 = 3CaF_2 + Na_3AlO_3 + 3H_2O.$$
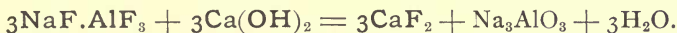
By removing the insoluble residue left by this reaction from the liquid, a separation of the aluminum from the fluorine is accomplished; but on the laboratory scale this separation is difficult to carry out on account of the colloidal nature of the residue. If filtration were resorted to, the pores of the filter would be immediately clogged with the gelatinous precipitate, so that the liquid would run so slowly, even with suction, that an undue length of time would be spent in accomplishing the separation. Therefore the method which will be employed is that of sedimentation after stirring up with a large amount of water. It must be borne in mind, however, that this device is adopted only to meet the requirements of laboratory practice, for on a commercial scale the expense of evaporating the large amount of water to obtain soda crystals, one of the by-products of the process, would be prohibitive. The separated sludge, consisting of calcium fluoride and all excess of calcium hydroxide, is of no great value, and will be discarded, although it could be used as a source of fluorine compounds; for example, hydrofluosilicic acid (H_2SiF_6).

From the clear solution of sodium aluminate the alumi-

num is precipitated by displacement of the weak aluminic acid from the salt by the action of the stronger carbonic acid,

$$2Na_3AlO_3 + 3H_2O + 3CO_2 = 3Na_2CO_3 + 2H_3AlO_3.$$
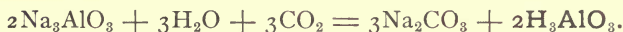
This precipitated aluminic acid, H_3AlO_3 (or, as more frequently named, aluminum hydroxide, $Al(OH)_3$), is also a very gelatinous substance, and can likewise only be separated, within a reasonable length of time, by means of sedimentation.

The aluminum hydroxide is treated with the calculated amount of sulphuric acid whereby the soluble salt, aluminum sulphate, is obtained. To this solution is added the calculated amount of potassium sulphate, and then the alum is allowed to crystallize.

The ideal conditions for obtaining large, clear crystals — which constitutes the beauty of this as a laboratory preparation — are, that a solution which is just saturated with alum may be slowly concentrated by spontaneous evaporation at a nearly constant temperature. Such conditions are found in industrial works, where the evaporation of the solution in large vats yields beautiful crystals, often of enormous size; but these necessary conditions are almost impossible to realize in a small laboratory preparation, and another method is adopted to give more rapidly and more surely the desired results.

100 grams water dissolve the given number of grams of
$K_2SO_4.Al_2(SO_4)_3.24H_2O.$

Temp. . .	$0°$	$5°$	$10°$	$15°$	$20°$	$25°$	$30°$	$40°$	$50°$	$60°$	$70°$
Grams . .	5.6	6.6	7.6	9.6	11.4	14.1	16.6	24	36	57	110

From the accompanying table it is seen that the solubility increases rapidly with the temperature. If a solution is saturated at $35°$ and then cooled to $15-20°$ about one-half of the alum will separate out, but ordinarily in the form of a mass of very minute crystals. In order to obtain large crystals during the cooling, three precautions are necessary : (1) A few minute crystals must be added to serve as nuclei for the crystallization before setting the solution to cool. (2) Dust must be excluded, since dust particles might serve as nuclei for the formation of a great number of minute crystals. (3) The cooling must take place very slowly in order that the crystal faces may be built up uniformly. This can be accomplished if the crystallizing dish is insulated by being covered with a glass plate and wrapped with a towel. If the solution set to crystallize is saturated at a much higher temperature than $35°$, it will be found that the crystallization will proceed so rapidly that it will be quite impossible, even if the above precautions are all observed, to obtain good crystals.

Procedure. — Slake 46 grams of quicklime and then mix in a large casserole with 250 cc. of water to make milk of lime. Stir into this 50 grams of finely powdered cryolite, and heat to boiling while stirring constantly. Continue boiling for an hour, adding water to replace that lost by evaporation and stirring sufficiently to avoid spattering. At the end of that time add a part of $1\frac{1}{2}$ liters of boiling water to the thick mass in the dish, and transfer it, together with the rest of the hot water, to a tall, wide-mouth, 2-liter bottle, and set aside to settle until the next period. The sludge should have settled so as to occupy not more than one-fifth of the volume of the liquid. Siphon off as much clear liquid as possible without drawing over any of the precipitate. Then add $1\frac{1}{2}$ liters more of hot water to the bottle, stir and again let settle, and draw off the clear

liquor. The residue in the bottle may be thrown away. Combine all the solution in a large bottle, and pass in carbon dioxide from a Kipp generator until all of the alumina is precipitated. Test to see if this is accomplished at the end of $\frac{1}{2}$ hour by stopping the carbon dioxide stream and letting the precipitate settle enough to pour off a little clear liquor into a beaker. Pass carbon dioxide into this for a few minutes; if no precipitation occurs it shows that all of the alumina has already fallen out of the solution. If a precipitate does appear, the treatment of the entire solution with carbon dioxide must be continued until all the alumina is thrown out. Then let the solution settle until the precipitate occupies less than one-sixth of the entire volume. Siphon off the clear liquid and evaporate it to dryness in a porcelain dish. Powder and preserve the sodium carbonate so obtained. Stir up the precipitate left in the bottle with $1\frac{1}{2}$ liters of hot water; let settle, and siphon off and discard the clear liquid, since it will not contain sufficient sodium carbonate to pay for its evaporation. To the suspension of aluminum hydroxide left in the bottle add 30 cc. of concentrated sulphuric acid, and warm, if necessary, to effect complete solution. Add 42 grams of potassium sulphate, and warm until dissolved. The solution should now be perfectly clear; if not, filter. If the volume exceeds 400 cc. evaporate to that bulk, and while still hot transfer it to the crystallizing dish (an 8-inch porcelain dish will answer). When cooled to 55–50°, drop 8 to 10 very small alum crystals into the solution, cover immediately with a glass plate, wrap the whole in a towel, and set where it will not be disturbed until the next exercise. Remove the few large crystals formed and preserve them. Evaporate the mother liquor not quite to $\frac{1}{2}$ its bulk (say $\frac{9}{16}$), and set this to crystallize in exactly the same manner as before. Add the crystals so obtained to the first lot.

Questions

1. Of what does the insoluble residue consist which remains after boiling the cryolite with milk of lime? When this is discarded after partial washing according to directions, what proportion of the soluble aluminum salt is lost with it? (Note that the actual solid material of the slime in question occupies an inappreciable volume as compared with the liquid in which it is suspended, even after the slime has been settling for several days. See Note 5 (*b*) on page 13.)

2. State what ions are produced by aluminum hydroxide (1) when it acts as an acid; (2) when it acts as a base. Compare its strength as an acid and as a base with that of other common electrolytes.

Define an *amphoteric* electrolyte.

3. *Experiment.* — Add a solution of sodium hydroxide, drop by drop, to 5 cc. of a solution of aluminum chloride, continuing until a considerable amount is added after the first effect is observed. Preserve the contents of the tube.

Repeat, using a solution of ammonium hydroxide instead of one of sodium hydroxide.

To the tube saved from the first part of this experiment add a solution of ammonium chloride.

Show how the difference in the degree of dissociation of the two bases accounts for the difference in the first two cases. State how it may also explain the result in the third case.

11. ALUMINUM SULPHIDE

This compound cannot be prepared in the wet way for the reason that it is decomposed by water. It is, however, readily prepared by the action of metallic aluminum upon lead sulphide at a high temperature.

Procedure. — Mix 133 grams of finely powdered galena [1] (lead sulphide ore) with 10 grams of granulated aluminum. Place in a small uncovered Hessian crucible, and heat as strongly as possible in a gas furnace until the charge in the crucible commences to react and a bright glow extends throughout the whole mass. Leave two or three minutes longer in the furnace at a white heat in order that the reaction may be entirely completed and that the charge may become quite liquid (a thin solid crust of aluminum oxide may form on the surface). Then pour into a dry,[2] clean iron pan; when cool detach the brittle aluminum sulphide [3] from the lead button and stopper the sulphide tightly in a test tube. The lead may be put in a box provided for scrap lead.

Questions

1. *Experiment.* — Drop a small lump of aluminum sulphide (at the hood) into a test tube of water. What is the gas formed and what is the insoluble residue left? What are the free acid and base into which the salt is resolved by the action of water? State the specific nature of both the acid and the base, which makes this reaction possible, instead of the reverse reaction (neutralization), which is the common one between an acid and a base.

2. If uncombined sulphur were used instead of lead sulphide as the source of sulphur for this preparation, suggest reasons why the process would be more difficult to control.

[1] A fairly pure sample of the mineral must be used in order to obtain good results.

[2] If the iron pan should chance to be moist, the heat of the charge would cause the formation of steam with explosive rapidity, thus throwing about the red-hot material.

[3] The aluminum sulphide must be handled entirely under the hood. None of it must be allowed to fall on the desks or floor of the open laboratory, because it reacts with the moisture of the air, producing a strong odor of hydrogen sulphide.

GENERAL QUESTIONS. II

Experiments

(The results observed are to be recorded in the laboratory notebook at the time the experiments are performed.)

1. Evaporate a little of an aluminum nitrate or aluminum chloride solution, and heat the residue carefully over a free flame until it is just dry. Examine the residue and test its solubility in water.

2. (*a*) Add ammonium hydroxide, drop by drop, to a solution of any soluble salt of aluminum until a precipitate has formed. (*b*) Then add a considerable excess of the reagent. (*c*) Collect a little of the precipitate of aluminum hydroxide on a filter, wash it entirely free from ammonia by means of hot water, and then test the reaction of the moist solid towards litmus.

3. Repeat (*a*) and (*b*) of Experiment 2, using sodium hydroxide instead of ammonium hydroxide. Divide the solution resulting from (*b*) into two parts: (*c*) To one part add hydrochloric acid, drop by drop, until a precipitate forms, then add an excess. (*d*) To the other part add ammonium chloride.

Questions

1. Boron and aluminum are the only members of the third group of the periodic system of the elements which are of common occurrence or of great importance. Turn to a table of the periodic system. From what you know of the regularities of this system what should you predict would be the valence of scandium, lanthanum, indium, thallium? Write the symbols of the sulphates of these elements. Find out from a text-book what chlorides of thallium are known to exist. Which one is characteristic of the position of

thallium in the third family ?   Is it of common occurrence for an element to display different valences?   Does this occur in the alkali or alkaline earth groups?

2. How readily is aluminum nitrate decomposed by heat (Experiment 1) ?   Compare it with the nitrates of the alkali and alkaline earth metals (General Questions, I). What is to be said of the stability of aluminum carbonate? How does aluminum compare with the alkali and alkaline earth metals as a base-forming element?

3. Compare aluminum hydroxide with sodium and magnesium hydroxides as regards solubility and degree of electrolytic dissociation.

4. Explain fully the behavior of aluminum hydroxide as an amphoteric substance (see Experiment 3).

5. In the third group of the periodic system the elements grow more strongly base-forming as the atomic weight increases and more strongly acid-forming as the atomic weight grows less. Thus with boron, base-forming properties are almost lacking and acid-forming characteristics are more strongly developed than with aluminum.

How can anhydrous boron chloride and anhydrous aluminum chloride be prepared?   How do each of these substances behave when treated with water, and how can the difference in the metallic character of the elements be judged from the difference in this behavior?

CHAPTER III

HEAVY METALS OF THE FIRST TWO GROUPS OF THE PERIODIC SYSTEM

The metals coming under this heading constitute the right hand or B Families in Groups I and II of the periodic system. They possess high specific gravities, and chemically they are far less active than the metals of the corresponding A Families,— they being not greatly, or not at all, affected by the atmosphere or by water. They are distinctly base-forming, in that their oxides yield fairly stable salts with the strong acids; but their basic properties are comparatively weak, and the oxides of some of them show very feeble acidic properties as well.

Copper, silver, and gold in Group I show a similarity to sodium and potassium principally in the fact that they form certain compounds of the same type, for example, M_2O and MCl. Zinc, cadmium, and mercury in Group II resemble calcium, barium, and strontium in that they form compounds of the types, MO, MSO_4, MCl_2, etc. In other respects the divergence in the properties of the elements of the A and B Families is at a maximum in these two groups.

12. CRYSTALLIZED COPPER SULPHATE (BLUE VITRIOL) FROM COPPER TURNINGS

On account of the fact that copper has not, like zinc, iron, etc., the power of displacing hydrogen from acids, it is not possible to dissolve it directly in dilute sulphuric acid. But although the metal itself is so difficult to affect with acids, nevertheless copper *oxide* is readily dissolved; and thus the problem becomes to convert copper into its oxide. The cheapest source of oxygen is the atmosphere, and on the commercial scale the usual method of obtaining copper sulphate from scrap copper is to allow dilute sulphuric acid to drip slowly over the latter, to which is given free access of air. Since, however, this method would be too time-consuming to apply on a small scale, nitric acid will be employed instead of air as the oxidizing agent.

$$3Cu + 2HNO_3 = 3CuO + H_2O + 2NO.$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$
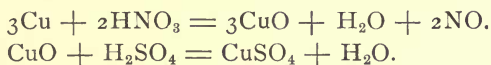
Procedure. — Heat 50 grams of copper turnings in an iron pan until all oily matter is burned and the metal has become coated with oxide. In a 500 cc. porcelain dish treat the ignited copper turnings with 300 cc. of dilute (1 : 4) sulphuric acid and 125 cc. of dilute nitric acid (sp. gr. 1.2). Warm in the hood over a Bunsen flame for 20 minutes; if any metallic copper remains undissolved, pour the solution off from it and dissolve it with a few cubic centimeters of fresh nitric acid and twice as much sulphuric acid. If the solution is not perfectly clear, filter it while still at the boiling temperature; then cool as rapidly as possible, stirring to get a crystal meal. Separate the crystals from the mother liquor by use of a Witt filter. Evaporate the mother liquor somewhat, and obtain a second crop

of crystals, throwing away the mother liquor from this crystallization. Dissolve all of the crystals by heating in their own weight of water; set the solution away to cool slowly, and after several hours remove the crystals which have formed and evaporate the remaining solution to obtain another crop of crystals.

Questions

1. Explain why copper will not dissolve in dilute sulphuric acid.

2. Write the equation for the reaction of copper with concentrated sulphuric acid. Analyze this reaction and show in what manner the copper is oxidized.

3. The quantities of sulphuric and nitric acid used were considerably in excess of what is theoretically necessary to react with the given amount of copper. Give reasons why the final product is not likely to be contaminated with copper nitrate or nitric acid or with free sulphuric acid.

4. How can copper sulphate be obtained from copper sulphide on a commercial scale?

13. CUPROUS CHLORIDE

Although copper itself is not readily oxidized, yet when oxidation is once induced it proceeds under most conditions at once to the "ic" state (corresponding to the oxide CuO). This is in accordance with the fact that cuprous salts are oxidized with the greatest readiness, so that, in the presence of any oxidizing agent powerful enough to oxidize metallic copper, any cuprous salt which might first be formed would instantly be oxidized to cupric. Therefore the readiest means of preparing a cuprous salt is to first prepare the cupric salt and then partially reduce it.

If metallic copper and cupric chloride be made to react, the former will act as a reducing agent, the latter as an oxidizing agent, and both will pass into the "ous" state of oxidation:

$$Cu + CuCl_2 = 2CuCl.$$
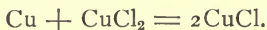
Cuprous chloride is soluble in a concentrated solution of hydrochloric acid with formation of a complex compound; the latter, however, is broken up on dilution with water, and insoluble cuprous chloride is precipitated. Cuprous chloride is so readily oxidized that, even in contact with moist air or suspended in water containing dissolved air, it is changed to a cupric salt:

$$2CuCl + 2HCl + O = H_2O + 2CuCl_2,$$

or
$$2CuCl + H_2O + O = 2Cu{<}^{Cl}_{OH}$$
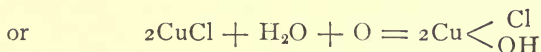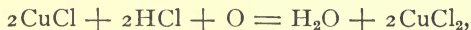
Hence a great deal of care will be necessary in washing and drying the cuprous chloride to prevent its becoming discolored in consequence of oxidation. When perfectly dry, however, or when covered with dry ether, the oxidation takes place very much more slowly.

Procedure. — Dissolve 43 grams of crystallized cupric chloride, $CuCl_2.2H_2O$, in 100 cc. of water and 100 cc. of concentrated hydrochloric acid (1.2). Place the solution, together with 25 grams of fine copper wire or clean copper turnings, in an Erlenmeyer flask; suspend a short-stemmed funnel in the neck of the flask to prevent in part the escape of acid vapors; raise the liquid to the boiling temperature, and keep it at that point, but without allowing it to actually boil appreciably, until the green color has disappeared.[1] If then a few drops of the liquid added to a test tube of water impart no blue color to it, the reaction is complete.

[1] If no impurities are present the solution becomes colorless. The color is more likely, however, to change from green to deep brown.

Filter the solution through asbestos (see Note 4 (d)), after first moistening the asbestos felt with concentrated hydrochloric acid. Pour the clear solution into a tall, common bottle containing 2 liters of water. Allow the white precipitate to settle, pour off the clear liquid, and stir up the precipitate again with 200 cc. of very dilute hydrochloric acid (about 1 cc. of the acid of 1.2 sp. gr. to 100 cc. of water). After the precipitate settles again, pour off the clear liquid, collect the precipitate on a Witt filter (Note 4 (b)), and wash it, first with very dilute hydrochloric acid, then with two successive portions of 15 cc. each of alcohol, and then with two portions of ether of like volume (Note 5 (a)). During the above treatment the precipitate should be kept out of contact with the air as much as possible, by keeping it covered with liquid all the time until it is freed from water by means of the alcohol and ether. After the ether has drained off, break up the caked cuprous chloride and leave it in a warm and dry place until the adhering ether has completely evaporated. Pulverize the product and stopper it tightly in a dry test tube. The product should be white. If it is discolored it must be dissolved in concentrated hydrochloric acid, poured into water, and washed and dried as before.

Questions

1. Does copper resemble silver more when in the cupric or the cuprous condition?

2. *Experiment.* — Expose a little cuprous chloride covered with water to the sunlight. What property is observed in which cuprous chloride is like silver chloride?

3. *Experiment.* — Place 2 to 3 grams of cuprous chloride in the bottom of a dry test tube. Have a stopper fitted to the tube, then fill it completely with ammonia water (sp. gr. 0.96) and immediately stopper it tightly, allowing no

air bubble to remain at the top.   Invert the tube a number
of times until the salt is dissolved.   At this point the solu-
tion should be nearly colorless, and it would be quite so
if the salt had been pure and air had been completely
excluded.   Unstopper the tube and pour quickly its con-
tents into a bottle of about 200 cc. capacity, and imme-
diately cork the latter air-tight.   Shake the bottle vigorously
for 3 minutes, then place the mouth under water and open
the cork.   From its quantity, infer what gas is absorbed out
of the air in the bottle.   What is the change in the condi-
tion of the copper salt which causes its change in color?
Formulate the reaction.

14. AMMONIUM AND COPPER SULPHATE

$$(NH_4)_2SO_4.CuSO_4.6H_2O$$
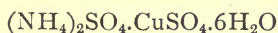
One example of the formation of a *double salt* has
already been illustrated in the preparation of alum, in
which there separates from a solution containing the two
simple salts K_2SO_4 and $Al_2(SO_4)_3$, not a mixture of the
crystals of each salt, but only a single kind of crystals
which are entirely different in nature from those of the
two simple salts.

The present preparation illustrates the formation of
another double salt.   An equal number of mols of copper
sulphate and ammonium sulphate are each dissolved in
water, and on mixing the solutions there are produced
crystals of the formula $(NH_4)_2SO_4.CuSO_4.6H_2O$.

Whether or not a double salt will separate from a mixed
solution, such as this one, depends upon the solubility rela-
tions existing among the various compounds capable of
formation.   In this case the double salt is considerably
less soluble than either of the simple salts.   On the other

hand, if saturated solutions of *sodium* sulphate and copper sulphate are mixed, no double salt will separate, but, on evaporation, a mixture of the crystals of the two simple salts will be obtained. Thus it appears that the double sulphate of sodium and copper is more soluble than the simple salts.

Procedure. — Weigh out 33 grams of ammonium sulphate and 62 grams of crystallized copper sulphate, and grind both salts together in a mortar until they are very finely powdered. Add the mixture to 250 cc. of water in a porcelain dish; raise the temperature to just 5° above the room temperature and keep it at that point during 10 minutes, while stirring all of the time with the stem of a thermometer. This gives a practically saturated solution of the double salt. Let the undissolved salt settle a moment and pour off the solution into another dish. With a little more water prepare in the same way a saturated solution of any residue that is left. Add a few drops of sulphuric acid to the entire solution, warm it to about 50°, and filter it, allowing the filtrate to run directly into an 8-inch dish. Smear a thin film of vaseline around the inside of the dish, at a little distance above the level of the liquid, in order to prevent crusts of the salt from *creeping* up over the edge of the dish. Set the solution away uncovered to crystallize in a place protected from the dust; and, before it has cooled to below the saturation temperature, seed it with eight or ten small crystals of the double salt. Allow the solution to stand until a large crop of crystals has formed. Drain the crystals, and, as they are slightly efflorescent, leave them spread out on an unglazed dish only until they are just dry. If only a small amount of mother liquor is left, it may be discarded.

It is a matter of considerable difficulty to obtain clear, well-formed crystals of this salt, especially if the laboratory

temperature varies a good deal. If the conditions are too unsatisfactory it is better to give up the attempt to get distinct crystals and to prepare, instead, a crystalline meal: Dissolve the same amounts of the two simple salts in 150 cc. of hot water; add a few drops of sulphuric acid; filter, and cool the solution rapidly in a flask while rotating it under the water tap. Drain the crystal meal on a Witt filter and dry it as directed above.

Questions

1. *Experiment.* — Dissolve a little of the salt in water. What ions does the solution contain? Make the ordinary tests for copper and sulphate ions. Does the double salt exist as such in solution?

2. Compare this double salt with the double cyanide of silver and potassium with regard to its tendency to dissociate. *Experiment.* — Make a little of the latter salt by adding to 1 cc. of silver nitrate solution just enough potassium cyanide solution to redissolve the precipitate which at first forms. Then in this solution of potassium silver cyanide test for simple silver ions by adding a little sodium chloride solution (not hydrochloric acid).

3. Find out by experiment whether the double salt $K_2SO_4.CuSO_4.6H_2O$, analogous to $(NH_4)_2SO_4.CuSO_4.6H_2O$, can be prepared.

15. AMMONIO–COPPER SULPHATE

$CuSO_4.4NH_3.H_2O$
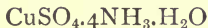
The copper and ammonium sulphate of the last preparation was produced by the combination of two simple salts and is therefore a so-called double salt. Ammonio-copper sulphate, on the other hand, is prepared from only one simple salt, copper sulphate, which in crystallizing is

caused to unite with four molecules of free ammonia and
one molecule of water, much in the same way as copper
sulphate unites with five molecules of water when it crys-
tallizes as blue vitriol. The molecules of ammonia would
appear to be bound to the copper atom of the salt rather
than to the sulphate radical, because when the salt is
dissolved in water the four ammonia molecules remain in
combination with the copper, giving the complex ion
$Cu(NH_3)_4^{++}$, while the sulphate radical gives only the
ordinary SO_4^{--}-ion. Thus we might say that this salt is
the sulphate of the ammonio-copper complex.

The salt is exceedingly soluble in water, and therefore,
in preparing it, use is made of its insolubility in alcohol.
The method adopted of allowing the alcohol to mix with
the aqueous solution only by slow diffusion is to insure the
formation of large, well-defined crystals.

Procedure. — Dissolve 25 grams of finely pulverized blue
vitriol in 84 cc. of dilute ammonium hydroxide (sp. gr. 0.96).[1]
Place 125 cc. of alcohol in a medium-sized common bottle.
Fill the stem of a small separatory funnel with water. In-
sert to the bottom of the alcohol, and run in 20 cc. of
water to form a layer beneath the alcohol to separate it
from the ammoniacal copper solution, which is next intro-
duced through the funnel. Allow no bubbles of air to be
sucked with the liquid into the stem of the funnel and thus
avoid mixing the layers. Set the bottle away for at least
a week, at the end of which time crystals 2 and 3 cm. long
will have formed. The alcoholic and aqueous layers have
not yet completely diffused into each other, and when they
are mixed a meal of very small crystals is precipitated.
Therefore pour the liquid all at once out of the bottle into
a clean beaker. The large crystals adhere to the inside
of the bottle. Remove them to a small dish; add 10 cc. of

[1] If the solution is not perfectly clear, it must be filtered through
asbestos (Note 4 (*d*)), since it dissolves filter paper (cellulose).

alcohol to which 1 cc. of ammonia has been added; stir thoroughly by rotating the dish, and pour off the alcohol, allowing it to carry with it any of the precipitate of small crystals. Repeat the washing with 10 cc. of plain alcohol and then with 10 cc. of ether. Spread the crystals on filter paper and leave them until they cease to smell of ether. Then put them up at once and stopper them tightly, since they give off their ammonia rather easily. Drain on a Witt filter the crystal meal formed in the beaker, and wash it on the filter (Note 5 (a)) with the same liquids as were used for the larger crystals. Preserve the large crystals and the crystal meal separately.

Questions

1. *Experiments.* — (a) What is the reaction between Cu^{++} and OH^--ions? Add sodium hydroxide solution, drop by drop, to a solution of copper sulphate until it is present in large excess. Save the solution.

(b) When ammonium hydroxide is added instead of sodium hydroxide, explain what successive reactions occur.

(c) Add ammonium chloride to the solution saved from (a) and explain the results.

(d) To 5 cc. of copper sulphate solution add 10 cc. of a 10 per cent. solution of tartaric acid; then add sodium hydroxide solution, as in (a), and compare the results with those in (a) and (b), but do not attempt to ascribe a definite formula to the complex compound formed.

2. *Experiments.* — (a) To 1 cc. of silver nitrate solution add sodium hydroxide until present in large excess.

(b) Repeat, using ammonium hydroxide instead of sodium hydroxide, and adding the reagent at first only a single drop at a time. Finally, after an excess of 5 cc. of ammonium hydroxide is present, test the solution with a little potassium chloride for the presence of silver ions. Compare the results with those in Experiment 1.

16. ZINC OXIDE

Zinc oxide is used as a white pigment, for which purpose it has the advantage of not turning black under the action of hydrogen sulphide. It can be obtained directly by burning metallic zinc, or from a soluble zinc salt by precipitating first a basic carbonate and then heating this to convert it into the oxide. Both zinc carbonate and zinc hydroxide are insoluble in water, but the basic carbonate is of still greater insolubility, and therefore precipitates more readily than the former two when the ions necessary to its formation are brought together. The simplest formula for the basic carbonate is

$$\begin{array}{c} Zn \diagdown OH \\ \diagup CO_3 \\ Zn \diagdown OH \end{array}$$
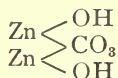
but the precipitate may be of very varying composition according to the conditions of its formation.

If zinc sulphate in solution is treated with sodium bicarbonate, pure zinc carbonate is precipitated, because a sodium bicarbonate solution contains but a minute quantity of OH^--ions. On the other hand, a sodium carbonate solution, in consequence of hydrolysis, contains a considerable quantity of OH^--ions, and thus it furnishes both the CO_3^{--} and OH^--ions necessary for the formation of basic zinc carbonate.

Zinc carbonate is decomposed by heat into zinc oxide and carbon dioxide.

Procedure. — Dissolve 50 grams of crystallized zinc sulphate (white vitriol) in 1.5 liters of hot water in a common 2-liter bottle, and add slowly, with stirring, a solution of 19 grams of anhydrous sodium carbonate in 250 cc. of hot water. Let the precipitate settle somewhat, and test, by adding a few drops more of sodium carbonate to the clear part of the solution, whether all the zinc has been precipitated. Let settle as much as possible (in 30 minutes perhaps to one-third or one-fourth of the bulk of the liquid).

Draw off the clear liquid and wash the remaining precipitate by decantation until it is calculated that it is contaminated with less than 0.1 per cent of the soluble sodium sulphate present at first (see Note 5 (b)). Finally, transfer the slime to a large, ordinary filter (Note 4 (c)), and allow it to drain over night. Without removing the pasty product from the filter open out the latter on an unglazed plate, and leave it on the steam table until the material is dry. Pulverize the basic zinc carbonate, and heat it in a small porcelain dish over a free flame until all the carbon dioxide has been driven off and the remaining zinc oxide is yellow when hot and pure white when cold.

Questions

1. Why could not the precipitate of basic zinc carbonate have been advantageously freed from the solution by means of a suction filter?

2. What test can you apply to prove that the zinc carbonate has been entirely converted into the oxide? Make the test.

3. Which is the more strongly basic, calcium oxide or zinc oxide? Which, then, could be more readily decomposed by heat, calcium carbonate or zinc carbonate?

4. *Experiment.* — To some solution of zinc sulphate add a solution of sodium hydroxide, drop by drop, until the precipitate first formed redissolves. How is zinc hydroxide similar to aluminium hydroxide in respect to its behavior towards strong acids and strong bases?

5. *Experiment.* — Knead up to a stiff paste about a gram of zinc oxide with a few drops of very concentrated zinc chloride solution, mold into a lump, and observe its condition at the end of half an hour. What chemical change occurs when this mixture hardens? Compare it with the change which occurs when plaster of Paris "sets."

Add a few drops of the concentrated zinc chloride solution to a tube of water. What is the precipitate?

17. MERCUROUS NITRATE

$HgNO_3.H_2O$
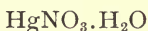
Like copper, mercury will dissolve in nitric acid, an oxide of mercury first being produced in consequence of the oxidizing action of nitric acid, and this oxide immediately reacting with the acid to form a salt. Mercury is capable of forming two oxides, Hg_2O and HgO, and two series of salts derived from these oxides in which the metal displays the valence I and II, respectively. In order to obtain the salt corresponding to the lower oxide, it is only necessary to keep an excess of mercury present throughout the action and not to allow the nitric acid to act too violently.

Procedure. — Treat 25 grams of mercury in a flask at the hood with 20 cc. of dilute nitric acid (sp. gr. 1.2), warming gently until no further action takes place. Allow to cool until the flask can be held in the hand, then pour the solution away from any remaining globule of mercury into a small dish, and leave to crystallize until the next day. Spread the crystals out upon an unglazed porcelain plate, and stopper them in a test tube as soon as dry.

Questions

1. Test the preparation for *mercuric* salt. Treat 0.5 gram of the preparation with 10 cc. of cold water. It will not dissolve to give a clear solution. Note the character of the residue. Add nitric acid, drop by drop, until a clear solution is obtained. By adding dilute hydrochloric acid, drop by drop, all of the mercurous salt can be precipitated, leaving any mercuric salt in solution. Fil-

ter ; test the filtrate for mercuric salt by means of hydrogen sulphide. Judge from the amount of the precipitate the quantity of mercuric salt, if any.

2. Explain why mercurous nitrate does not dissolve completely in pure water and what is the character of the residue. How do a few drops of nitric acid aid in the solution ?

3. Explain the use of hydrochloric acid in separating mercuric from mercurous salt.

18. MERCURIC NITRATE

When mercury is heated with an excess of nitric acid, mercuric nitrate is produced. This salt is exceedingly soluble in water, and it can only be crystallized with a good deal of difficulty. When a solution of it which contains an excess of nitric acid is evaporated, it becomes a thick, heavy sirup, which by further driving off of nitric acid and water becomes a pasty mass, due to formation of small crystals of basic nitrate, $Hg<^{NO_3}_{OH}$. If the materials taken for the preparation of this salt are pure, the product can contain no other foreign matter than an excess of nitric acid ; consequently, in view of the difficulty of obtaining good crystals, it is convenient to preserve the salt in this pasty condition.

Procedure. — Heat 25 grams of mercury in a flask with 48 cc. of dilute nitric acid (sp. gr. 1.2) until it is all dissolved. Test a drop of the solution by adding to it in a test tube $\frac{1}{2}$ cc. of cold water and a drop of dilute hydrochloric acid. A precipitate will probably form, in which case add 10 cc. of concentrated nitric acid to the flask and boil until a precipitate is no longer obtained when tested as above. Pour the solution into a dish and evapo-

rate over a very small free flame until the liquid has assumed a sirupy consistence and crystals just commence to form on the surface. Then remove the whole mass to a small, wide-mouth sample bottle, which has previously been weighed; let it cool and stopper it.

Questions

1. To prepare a solution of this salt for use as a laboratory reagent, explain why it is necessary to add a small quantity of nitric acid. (Compare with Questions 1 and 2 under Mercurous Nitrate.)

2. *Experiment.* — To a solution of mercuric nitrate add a little hydrochloric acid. Now add a little stannous chloride solution. What is the precipitate, and what change in the valence of mercury must have occurred before it could form?

19. MERCURIC SULPHOCYANATE

In most of its properties the sulphocyanate radical resembles the halogens, with which it is often classed, in the same manner that the ammonium radical, NH_4, is classed with the alkali metals. Thus potassium sulphocyanate, KSCN, yields the ion SCN^- just as potassium chloride yields the ion Cl^-. Mercuric sulphocyanate is insoluble in water, and can be produced by bringing together equivalent quantities of solutions of mercuric nitrate and potassium sulphocyanate, but if an excess of either of these reagents is used the precipitate dissolves in it with the formation of a complex soluble compound. While by a consideration of the Mass Law one would predict that an excess of either ion would cause a decrease in the solubility of the salt $Hg(SCN)_2$, another factor nevertheless

comes into play, namely, the tendency of the molecule $Hg(SCN)_2$ to combine either with Hg^{++} or SCN^--ions to form complex ions, which under the conditions given are capable of remaining in solution. Similar phenomena are not of infrequent occurrence where a given amount of a reagent will cause a precipitate, while an excess will cause the precipitate to redissolve. For instance, carbon dioxide gas, if passed into a solution of calcium hydroxide, causes a white precipitate, but more of the gas causes the precipitate to redissolve. A very neat expedient may be adopted in this preparation to show when the proper amount of reagent has been added, as follows: ferric sulphocyanate, $Fe(SCN)_3$, is a soluble substance which has an intensely red color. If to a given solution of mercuric nitrate a few drops of a ferric salt solution are added, and then to this is gradually added a solution of potassium sulphocyanate, the SCN^--ions will unite with the Hg^{++}-ions so long as any of the latter are present, the solution remaining colorless and the precipitate $Hg(SCN)_2$ forming towards the end; but so soon as the Hg^{++}-ions are exhausted, then the SCN^--ions unite with Fe^{+++}-ions, producing the red compound, and the appearance of the red color is the indication to stop.

Mercuric sulphocyanate has the peculiar property that when ignited it burns with the production of a very voluminous coherent ash, which, from the form which it assumes, is called "Pharaoh's Serpent." It should not be burned in an open room because of the production of mercury vapor, which is poisonous.

Procedure. — Dissolve the mercuric nitrate obtained in the last preparation in 1 liter of water, adding enough nitric acid to prevent the formation of any basic salt. To this add 10 drops of a ferric chloride solution; then add gradually, with constant stirring, a solution of 25 grams of potassium sulphocyanate in 500 cc. of water until a red

color appears and persists after stirring. Collect the precipitate on a Witt filter, and dry it upon an unglazed plate.

The dried salt may be made into the so-called Pharaoh's serpent eggs by kneading it with 1.5 grams of dextrine dissolved in 5 cc. of water to obtain a stiff paste, molding this into small cones or pellets, and allowing them to dry.

Questions

1. Observations made in the course of this preparation are sufficient to decide whether ferric sulphocyanate, $Fe(SCN)_3$, is an ionized or un-ionized substance. Explain.

2. Find out what is the degree of dissociation of the soluble halides of mercury, i. e., $HgCl_2$, $Hg(CN)_2$. Do these salts form in this respect any exception to the general rule regarding the ionization of salts?

3. Describe at least three instances which have previously fallen under your observation in which a reagent in limited amount will give a precipitate, but, added in excess, will cause the precipitate to redissolve.

GENERAL QUESTIONS. III

HEAVY METALS OF THE FIRST TWO GROUPS OF THE PERIODIC SYSTEM

Experiments

(The results observed are to be recorded in the laboratory notebook at the time the experiments are performed.)

1. Heat a little dry copper carbonate rather gently in a test tube by shaking it in a Bunsen flame until the color has completely changed to black. Then test the residue for carbonate by adding hydrochloric acid.

2. To solutions of copper, silver, zinc, cadmium, and mercury salts, in separate test tubes, add sodium hydroxide

until a precipitate forms in each case, and then add a considerable excess of the reagent.

3. Repeat Experiment 2, using ammonium hydroxide instead of sodium hydroxide.

4. Place small pieces of copper wire in solutions of silver and mercury salts. Note whether any metal is precipitated on the surface of the copper, and test the solutions by adding an excess of ammonia to prove whether any copper has passed into solution. Place pieces of zinc in a copper salt solution, let it stand for some time with frequent shaking, and find out whether all of the copper can be precipitated by means of the zinc.

Questions

1. The heavy metals of the first two groups of the periodic system show certain similarities to the alkali and alkaline earth metals with respect to the type of compounds formed. In this way their positions in the same groups are in a measure justified. They show, however, more divergencies in their properties, and on this account they fall naturally into separate families within the groups.

Which of these metals are capable of showing different valences? Give the symbols of the chlorides in which the valence of the metal is characteristic of its position in the group.

2. Compare the stability of copper carbonate (see Experiment 1) with that of potassium carbonate; that of zinc carbonate with that of calcium carbonate. How do the heavy metals of the first two groups compare as regards basic strength with the alkali and alkaline earth metals? How do they compare with aluminum in this respect?

3. What in general terms can be said about the solubility of the hydroxides of copper, silver, zinc, cadmium, and mercury (Experiment 2)? Are the salts of these metals much or little hydrolyzed in aqueous solution?

What does this indicate in regard to the base-forming characteristics of the metals?

4. Which of the hydroxides of these metals are amphoteric? (Experiment 2.)

5. Give the formulæ of the soluble ammonio-salts of copper, silver, and zinc. (Experiment 3.)

6. Arrange the metals of Family B in Groups I and II in the order of their electrolytic solution tension (Experiment 4). Compare Families A and B in each group with respect to this property.

CHAPTER IV

ELEMENTS OF THE FOURTH GROUP OF THE PERIODIC SYSTEM

This group stands in the middle of the Periodic Table of the elements, and in it the difference in properties between the elements of Family A and Family B is at a minimum. As in the case of Group III, therefore, the whole group is considered under one heading.

The only elements of this group which are to be especially considered are carbon, silicon, tin, and lead. Carbon and silicon are the first two members and are exclusively acid-forming elements, although the acids formed are not strong ones. Tin and lead are the last two members of Family B and are in the main base-forming; they are comparable in this respect with the heavy metals already considered under Groups I and II. It is a characteristic of this group that the acid-forming properties are most pronounced in the elements of low atomic weight, while the base-forming properties are most pronounced in the elements of high atomic weight.

Titanium, although it is a fairly abundant constituent of the earth's crust, is an element of comparatively little importance, and is never taken up in connection with the more common elements.

Cerium and thorium, the heaviest two elements of Family A, have acquired some importance on account of the use of their oxides in incandescent gas-lighting mantles.

20. STANNOUS CHLORIDE $(SnCl_2.2H_2O)$

This salt can be prepared by the action of hydrochloric acid upon metallic tin. Since, however, the action would be exceedingly slow, it may be hastened by the addition of a very small quantity of nitric acid, which will oxidize the tin. Nitric acid is ordinarily, by its action upon a metal, reduced only to the oxide NO; but in the course of this preparation no red fumes of oxides of nitrogen will be found to escape, because, under the influence of tin and stannous chloride, the reduction does not stop at nitric oxide, but continues to the lowest possible step, which is ammonia or in this case its salt, ammonium chloride. Stannous salts are, under the influence of the oxygen of the air, oxidized quite readily to stannic; to prevent this happening during the evaporation of the solution, an excess of metallic tin is kept in the liquid.

Procedure. — Place 100 grams of feathered tin in a large casserole, cover with 175 cc. of concentrated hydrochloric acid (sp. gr. 1.2), and add (at the hood) 25 cc. of ·dilute nitric acid (sp. gr. 1.2), a little at a time, during a period of 10 minutes. Then concentrate the solution, by boiling over a free flame, to a volume of 90–100 cc., at which point a crystal scum will form on blowing on the surface of the hot liquid. There should still be left a small amount of undissolved metal. If at any time during the evaporation all the tin becomes used up, add a little more. Prepare an asbestos filter (Note 4 (*d*), page 10), moisten it with concentrated hydrochloric acid, and filter the concentrated stannous chloride solution before it has cooled to below 60–70°. Finally, rinse out the casserole with 15 cc. of concentrated hydrochloric acid and pour this liquid through

the filter, letting it mix with the main part of the solution. If during the filtration the liquid stops flowing, due to crystals separating in the filter, add 5–10 cc. of boiling water. Pour the solution into a 6-inch evaporating dish, and leave it to evaporate slowly at room temperature in a place exposed to the air but protected from dust. (The solubility of stannous chloride decreases very rapidly with decreasing temperature. Hence it is advantageous to carry out the crystallization in as cool a place as possible.) When a good crop of crystals has formed, pour off the liquid into another dish, spread the crystals on an unglazed dish, and allow them to dry. It is to be remembered that stannous chloride is extremely soluble in water and that the composition of the mother liquor is not far different from that of the crystals of $SnCl_2.2H_2O$ which separate. Heat the remaining solution carefully just to the boiling temperature, but do not allow it to boil more than a moment. In this way sufficient water and hydrochloric acid are expelled to allow another crop of crystals to form.[1] Set the solution aside to cool and evaporate, as before, and collect another crop of crystals. By repeating this process once or twice more, almost the entire mother liquor should be used up and nearly the calculated yield of stannous chloride should be obtained.

Questions

1. Explain why during this preparation no red oxides of nitrogen are seen to escape in consequence of the reduction of nitric acid by the metal.

If nitric acid is reduced to NH_3, show how many more

[1] If too much hydrochloric acid is expelled by the evaporation and an indistinctly crystalline precipitate of basic salt separates on cooling, add a few drops of hydrochloric acid, redissolve the salt by warming, and set the solution to crystallize again, seeding it when cold with a small crystal from the first crop.

equivalents of oxygen it will yield for the oxidation of the tin than if it were reduced only to NO.

Experiment. — To test for the presence of ammonium salt in the product, take about 1 gram of the crystals; dissolve in 10 cc. of water in a small beaker. Add sodium hydroxide solution until the precipitate first formed redissolves. Place over the beaker a watch glass, on the under side of which is stuck a piece of moistened red litmus paper. Place some cold water in the hollow of the watch glass, and warm the solution in the beaker very gently. What will, if it occurs, indicate the presence of ammonium salt, and why?

2. *Experiment.* — Dissolve 1 gram of stannous chloride crystals in 1 to 2 cc. of cold water. Then add a considerable amount of water. What is the precipitate? What can be added to prevent its formation?

3. *Experiment.* — To a cold solution of stannous chloride add sodium hydroxide until it has redissolved the precipitate first formed. Write the reaction. Save the solution.

4. *Experiment.* — Pour the solution saved from Experiment 3 over a little bismuth hydroxide on a filter paper. (The latter can be precipitated for the occasion.) Compare the action with that of stannous chloride on mercuric chloride. (See Experiment 2 under Mercuric Nitrate.)

5. *Experiment.* — Prepare a very concentrated cold solution of sodium stannite: Dissolve 1 gram of stannous chloride in 1 cc. of water. Dissolve a small lump of sodium hydroxide in its own weight of water, and add this solution, a drop at a time, to the first solution — cooling all the while under the water tap — until the precipitate at first formed redissolves. Then heat the solution. Compare the action with that in Experiment 4.

6. In preparing a solution of stannous chloride for a laboratory reagent, what is the necessity of adding free

hydrochloric acid and of placing a piece of metallic tin in the bottle?

21. STANNIC SULPHIDE (MOSAIC GOLD)

Stannic sulphide, SnS_2, is the higher sulphide of tin, and can be prepared by direct combination of the metal or, still better, of the lower sulphide, SnS, with sulphur. Under ordinary conditions these two substances will not react at a temperature below that which will decompose stannic sulphide. If, however, they are mixed with ammonium chloride the presence of this substance makes possible the combination at a lower temperature, and also, since it absorbs heat by its volatilization, it prevents the temperature from rising too high. The stannic sulphide formed in this way appears as soft, glistening, yellow crystals. It is used as a bronzing powder, and is known under the name of mosaic gold. In physical properties it is very different from the stannic sulphide which can be precipitated by hydrogen sulphide from a solution of stannic chloride.

Procedure. — *Stannous Sulphide.* Weigh out 40 grams of commercial stannous chloride, $SnCl_2.2H_2O$, into a casserole, add 25 cc. of concentrated hydrochloric acid (1.2), and warm the mixture gently until the salt is dissolved. Dilute the solution to 1,500 cc. with boiling water in a 2-liter common bottle, and pass hydrogen sulphide (generated in a small generator bottle from ferrous sulphide, broken into small lumps, and hydrochloric acid; the gas is not to be taken from the laboratory taps) into the solution until all of the tin is precipitated. To test for complete precipitation, filter off a small sample and treat it with more hydrogen sulphide. Wash the precipitate twice by decantation (Note 5 (*b*), on page 13), then collect it on a filter

without suction (Note 4 (*c*)); wash it twice on the filter with hot water from the wash bottle, and allow it to drain thoroughly. Without tearing the filter, remove it carefully from the funnel and spread it out on an unglazed plate with the precipitate still on it. After drying it thoroughly at the steam table, separate the brittle lumps of stannous sulphide from the paper and powder them.

Stannic Sulphide. — Grind together thoroughly 20 grams of the stannous sulphide just prepared, 10 grams of sulphur, and 8 grams of ammonium chloride. Bring the mixture into a small flask and place it on a sand bath, forcing it down as much as possible into the sand. Cover the mouth of the flask with an inverted test tube or small beaker, and protect the sides with asbestos paper. Heat the sand bath for 2 hours, at first rather moderately, and finally so that the bottom of the iron pan is a bright red in the center. Cool, break the flask, and preserve the layer of stannic sulphide which is found at the bottom.

Questions

1. *Experiment.* — Prepare a little stannic sulphide by precipitation with hydrogen sulphide from a solution of stannic chloride. Compare this with the stannic sulphide prepared above as regards its solubility in hydrochloric acid.

2. *Experiment.* — In each of two test tubes place about ¼ gram of powdered stannous sulphide, and fill each tube to the same height, about half full, with *colorless* ammonium sulphide. To one tube add a few small lumps of roll sulphur. Bring the contents of both tubes just to the boiling temperature, and then let both stand with occasional shaking and further gentle heating until the black stannous sulphide in one tube has dissolved. Pour off about 2 cc. of the clear liquid from this tube, dilute it with 15 cc. of water, and just acidify the solution with hydrochloric acid.

Sodium sulphostannite is so unstable a salt that even if it could be formed it would revert at once into sodium sulphide and stannous sulphide. Sodium sulphostannate is a more stable salt.

Explain the reaction and write the equation for the formation of the sodium sulphostannate. Give the equation for the reaction with hydrochloric acid.

Explain the analogy between the oxy-salt sodium stannate and the sulpho-salt sodium sulphostannate.

22. STANNIC CHLORIDE (ANHYDROUS)

Anhydrous stannic chloride, $SnCl_4$, is a mobile and volatile colorless liquid with a boiling point at 114°. It fumes very strongly in the air; with water in moderate amount it forms crystalline compounds, but with more water it dissolves to a clear solution. It is prepared by the action of dry chlorine gas upon metallic tin.

Apparatus. — This preparation is only to be attempted if four consecutive hours are available in the laboratory, and even then, the apparatus should be assembled as much as possible at a previous exercise.

Arrange a chlorine generator, the gas from which is to be passed through, first one wash bottle containing water, and then two wash bottles containing concentrated sulphuric acid. Place 150 grams of tin in a tubulated retort, and place the retort on a sand bath. The neck of the retort should pass into a long condenser, and the latter should empty into a 200 cc. distilling flask, in which has been placed some tin foil. Connect the side arm of the flask with a bottle containing sodium hydroxide solution to absorb the waste chlorine. The tube entering the bottle should not dip into the liquid, but should reach down to near its surface; a safety tube should be supplied, and

the exit tube should dip into a solution of sodium hydroxide in another bottle. Into the retort should be fitted the tube supplying chlorine from the generator and wash bottles, and this should reach nearly to the center of the surface of the tin, which is to be melted before the action is started. Glass tubing is to be used throughout, and where connections are made with rubber the ends of the glass tubes should be brought close together. Before beginning to generate the chlorine, the whole apparatus must be proved to be tight, so that none of this gas can escape into the laboratory.

Procedure. — Melt the tin. Commence the generation of chlorine and regulate it so that the tin in the retort can be seen to burn quietly, but do not allow this action to become too violent. Continue the action until all the tin has disappeared and the tin tetrachloride has been caught in the receiving flask. Remove the neck of the retort from the condenser, and insert instead a stopper with a tube leading to the bottles already used for absorbing waste chlorine. Close the side arm of the receiving flask and, with the condenser still in the same position, boil the tin tetrachloride until it is colorless (it contains a large amount of dissolved chlorine and, on boiling, this reacts with the tin foil). Change the position of the flask and condenser, and distill the tin tetrachloride into a flask whose neck has been drawn down so that it can be readily sealed off. During the distillation the flask should not be open to the air, but should be connected by a tube to the absorbing bottles already used. When the liquid is all distilled, seal the neck of the flask at a blast lamp, so that the preparation can be preserved out of contact with the air.

Questions

1. What is the purpose of the wash bottles as arranged for the chlorine gas?

2. Compare the physical properties of the tetrachlorides of carbon, silicon, tin, and lead.

How do these substances behave in presence of water, and what information does this give as to the metallic character of the four elements?

23.   LEAD NITRATE

Lead nitrate is one of the most readily prepared salts of lead, since it is of moderate solubility and can be obtained in well-formed anhydrous crystals $(Pb(NO_3)_2)$. In it lead appears in its usual state of oxidation, which corresponds to that of the oxide PbO; indeed, the salt is actually prepared by treating this oxide (litharge) with nitric acid.

A saturated solution contains for each 100 grams of water the given number of grams of lead nitrate

Temperature	0°	10°	18°	25°	50°	100°
$Pb(NO_3)_2$	36	44	51	56	79	127

Procedure. — Take 50 grams of litharge. Calculate the amount of nitric acid which would be necessary to convert it into lead nitrate and the amount of water needed to dissolve the salt which is thus formed. Proceed to prepare lead nitrate, striving to obtain good crystals of as large a size as possible.

Questions

1. Explain why lead nitrate should be less soluble in dilute nitric acid than in pure water.

2. Add a few drops of ammonium hydroxide to 1 cc. of lead nitrate solution. Then add an excess of the reagent. Repeat, using sodium hydroxide instead of ammonium hy-

droxide. Give equations and explain the amphoteric character of lead hydroxide.

3. Are lead salts (nitrate or chloride) appreciably hydrolyzed in aqueous solution? Compare the basic strength of lead hydroxide with that of aluminum hydroxide.

4. Precipitate a little lead chloride by adding hydrochloric acid to a solution of lead nitrate. Describe its properties and compare them with those of lead tetrachloride (text-book). To what oxide of lead does lead tetrachloride correspond?

24. LEAD DIOXIDE

As already stated, the most frequently occurring and the most stable compounds of lead are those derived from the oxide PbO. Under certain conditions, however, this oxide, or any salt derived from it, may be converted into the higher oxide PbO_2. Thus if a solution of lead acetate is made alkaline and is then treated with an oxidizing agent, such as chlorine, the dioxide results. On account of the disagreeableness of using chlorine gas in the laboratory, bleaching powder, which exerts practically the same oxidizing action, will be substituted for it. The precipitate finally obtained after the bleaching powder has acted contains the greater part of the lead in the form of lead dioxide; but it may also contain a small residue of unoxidized lead, as $Pb(OH)_2$, as well as calcium hydroxide from the bleaching powder and possibly the salts calcium plumbate and calcium plumbite, $CaPbO_3$ and $CaPbO_2$. By treating this precipitate with nitric acid everything except the lead dioxide is dissolved or decomposed, and practically pure lead dioxide remains.

Procedure. — Dissolve 100 grams of lead acetate in 200 cc. of cold water in a 750 cc. casserole; add a solution of 21

grams of sodium hydroxide dissolved in 100 cc. of water, stirring well, and into the mixture, which should not be warmer than 30°, stir a paste made by rubbing 60 grams of bleaching powder in a mortar with a little water. Warm the mixture slowly to the boiling temperature, stirring frequently, and finally boil it for 10 minutes. Transfer the contents of the casserole to a 2-liter common bottle and wash the precipitate by decantation with cold water (see Note 5 (b) on page 13) until the wash water gives no test for chlorine ions. Then transfer the remaining slime again to a casserole, add 250 cc. of nitric acid (1.2), and boil it for 10 minutes. Wash the residue of lead dioxide by decantation until the wash water is no longer acid; transfer the product to a filter and let it drain without suction (Note 4 (c) on page 9). After the lead dioxide has drained, remove the filter and contents carefully from the funnel, unfold the filter, and spread it on an unglazed plate on the steam table to dry. When completely dry, detach the lumps of lead dioxide from the paper, and pulverize them in a mortar.

Questions

1. *Experiment.* — Add sodium hydroxide to a solution of a lead salt, and observe with what readiness the precipitate redissolves in an excess of the reagent.

Give reactions, and compare $Pb(OH)_2$ with $Al(OH)_3$ as regards the strength of their acidic properties.

2. Write the reaction between sodium plumbite and chlorine in the production of lead dioxide; between sodium plumbite and bleaching powder.

3. Show the relation among ortho-plumbic acid, meta-plumbic acid, and lead dioxide. Give the symbol of sodium meta-plumbate; of calcium ortho-plumbate.

4. In view of the following experiment, why could not lead dioxide have been prepared equally well by treating

a solution of lead chloride, containing also free hydrochloric acid, with chlorine? *Experiment.* — Drop a grain of lead dioxide the size of a pinhead into $\frac{1}{2}$ cc. of hydrochloric acid, and warm until dissolved. What odor is observed? Cool the liquid and observe the character of the precipitate.

5. Compare the reaction of lead dioxide and of lead monoxide upon hydrochloric acid.

6. Compare the action of lead dioxide upon hydrochloric acid with that of manganese dioxide.

7. Why should not lead dioxide and manganese dioxide dissolve in nitric acid as well as in hydrochloric acid?

25. RED LEAD, Pb_3O_4

Of the oxides of lead, the monoxide PbO is the most stable when heated to a high temperature, and in fact all of the other oxides are converted into this one when they are heated strongly in contact with the air. At a moderate heat, however, the monoxide is capable of taking on more oxygen from the air until the composition approximates that of the formula Pb_3O_4. This substance is not to be regarded as a simple oxide of lead, but rather as a compound of PbO and PbO_2, in which the monoxide is the basic component and the dioxide the acidic. It may thus be regarded as the salt, lead orthoplumbate, $2PbO.PbO_2 = Pb_2(PbO_4)$. This view is strengthened by the behavior of the substance when treated with nitric acid — part of the lead dissolves to give lead nitrate, while the other part is left as lead dioxide,

$$Pb_2(PbO_4) + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + H_4(PbO_4)$$
$$H_4PbO_4 \rightarrow PbO_2 + 2H_2O.$$
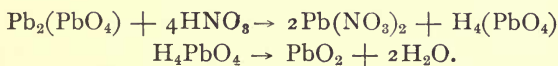
The following procedure should yield a product of nearly the composition Pb_3O_4. This substance, under the commercial name of minium, finds use as a red pigment.

Procedure. — Spread 25 grams of lead monoxide in a
thin layer on an iron or aluminum plate 2–4 mm. thick.
Either use the variety of lead oxide which has not been
fused and is known under the name of massicot, or use lead
carbonate, which on being heated yields a very pure and
finely divided lead monoxide. Heat the lead oxide over a
ring burner so adjusted that the flames do not quite touch
the metal plate.   The latter must be kept just below a per-
ceptible red heat.   Continue the heating for 2 hours or
more and turn over the powder frequently with an iron
spatula.   When the change is complete, the product is dark
brown when hot, a bright scarlet-red when partly cooled,
and a somewhat less brilliant red when entirely cold.

Questions

1.   If it is assumed that Pb_2O_3 and Pb_3O_4 are lead
metaplumbate and lead orthoplumbate, respectively, write
formulæ to express these facts.   Write the formulæ of the
corresponding meta- and ortho-plumbic acids.

2.   *Experiment.* — Boil a little of the red lead with nitric
acid.   What is the residue, and what soluble salt is formed ?
Test the solution by diluting and adding a few drops of
sulphuric acid.

3.   *Experiment.* — Heat a little of the red lead to a dull
red heat on a thin piece of iron.

GENERAL QUESTIONS.   IV

ELEMENTS OF THE FOURTH GROUP OF THE PERIODIC SYSTEM

Experiments

(The results observed are to be recorded in the laboratory note-
book at the time the experiments are performed.)

1.   Heat a little lead carbonate gently by shaking it in
a test tube in a Bunsen flame until its color has changed

entirely from white to brownish yellow. After cooling, test the residue for carbonic acid by adding dilute nitric acid.

2.   Heat a little piece of tin in a casserole with some nitric acid until the metal has all been converted into a white powder. What is the powder?

3.   Boil a little litharge, PbO, in a test tube of water for a few minutes. Then test the solution with red litmus. Also filter off some of the clear solution and test it for lead by adding hydrogen sulphide water.

4.   To a little diluted stannous chloride solution add sodium hydroxide solution, drop by drop, until a heavy white precipitate has formed, then add it in considerable excess. Repeat, using a solution of a lead salt instead of stannous chloride, and observe how great an excess of sodium hydroxide is necessary to redissolve the precipitate at first formed.

Questions

1.   Of the elements of the fourth group only four need be given especial consideration, namely, carbon, silicon, tin, and lead. What is the characteristic valence of the elements of this group? Give the symbols of all the oxides of each of these elements, and indicate in each case whether the substance is gaseous liquid or solid. In the same way give the symbols and indicate the state of aggregation of the chlorides of these elements when in the pure state.

2.   Is tin carbonate capable of existence? What is the stability of lead carbonate? (See Experiment 1.) Are salts of carbon and silicon, such as sulphates or nitrates, capable of existence? How does the strength of the base-forming tendency change in this group in going from carbon to lead?

3.   Is a higher carbonate of lead than $PbCO_3$ capable of existence? Can lead tetranitrate, $Pb(NO_3)_4$, be prepared? How does lead tetrachloride behave when treated with a large amount of water? Which of the oxides of tin

is capable of forming the corresponding nitrate and sulphate? (See Experiment 2.) Explain how these facts show whether the monoxides or the dioxides of lead and tin are the more strongly base-forming.

4. Discuss the solubility and the degree of the electrolytic dissociation of lead hydroxide (Experiment 3). Discuss the amphoteric character of $Sn(OH)_2$ and $Pb(OH)_2$ (Experiment 4).

5. How may sodium sulphostannate be prepared? What relation does it bear to sodium stannate?

6. Of the five distinct oxides of lead described in the text-books, which are the salt formers, *i. e.*, which are the simple basic or acidic anhydrides?

CHAPTER V

ELEMENTS OF THE FIFTH GROUP OF THE PERIODIC SYSTEM

In this group, as in Groups III and IV, the difference in properties between the elements of Families A and B is not so striking as in Groups I and II (or as in Groups VI and VII). Consequently the whole group is considered under the same heading. But it is also true that the elements of Family A, that is, vanadium, columbium, and tantalum, are of comparatively infrequent occurrence, and are given no attention in this course. On the other hand all of the elements of Family B are of frequent occurrence and considerable importance.

The characteristic valence of the group is five, corresponding to the oxide M_2O_5, but the elements likewise all exhibit a valence of three in the oxide M_2O_3. It is noteworthy that the valence is nearly always either three or five.

It is true in this group, as well as in Group IV, that the acid-forming properties are most marked in the elements of low atomic weight (nitric acid is one of the strongest acids), and decrease with increasing atomic weight; whereas the base-forming properties are most strongly developed with the elements of high atomic weight.

26. ORTHO-PHOSPHORIC ACID. H_3PO_4

A rather impure grade of phosphoric acid can be obtained from natural calcium phosphate by decomposition with sulphuric acid, but a pure product may be most readily obtained by oxidizing phosphorus by means of nitric acid.

The solution first obtained by the action of dilute nitric acid upon phosphorus contains a considerable quantity of phosphorous acid, H_3PO_3; but upon boiling down this solution, a point is reached at which a rather strong reaction takes place, which consists of an oxidation of the phosphorous to phosphoric acid by means of the nitric acid still present.

Commercial phosphorus often contains a small quantity of arsenic. This on the treatment with nitric acid is oxidized to arsenic acid, which, unless removed by hydrogen sulphide, would contaminate the preparation of phosphoric acid.

Phosphorous acid may always be present in the product in case the oxidation with nitric acid has not been complete, and its presence may be detected by its ability to reduce silver nitrate and give a black precipitate of metallic silver,

$$H_3PO_3 + 2AgNO_3 + H_2O = 2HNO_3 + 2Ag + H_3PO_4.$$

Procedure. — Place 275 cc. of nitric acid of sp. gr. 1.2 in a 2-liter, round-bottom flask. Weigh out 30 grams of red phosphorus, and at the hood add 10 grams to the nitric acid in the flask. Warm by placing the flask in a pail of hot water just until red vapors begin to appear ; then stand the flask on a wooden ring, and place a large funnel in its neck to condense and allow to drip back at least a part of the vapors. After the action has nearly ceased, add a little more of the phosphorus and again wait until action has almost stopped, and so on until all of the phosphorus is used. When the action following the last addition of phos-

phorus has somewhat moderated, add 20 cc. of concentrated nitric acid (sp. gr. 1.42). Boil the solution in a casserole until it is considerably concentrated and a rather violent reaction is observed to take place with evolution of red fumes. When this action has ceased, the remaining solution is poured into a flask, diluted to about a liter with water, saturated with hydrogen sulphide gas, stoppered, and allowed to stand over night. If the next morning the contents of the flask smell strongly of hydrogen sulphide, the precipitate of arsenic sulphide is filtered off; if not, the solution is again treated with hydrogen sulphide in the same manner as before. Evaporate the filtrate until its temperature has risen to $125°$. Test a few drops for phosphorous acid by diluting with a little water, adding some silver nitrate, and warming. If any is found add 20 cc. of nitric acid to the solution and warm it. Transfer the solution to a small casserole and evaporate it over a very small flame until a thermometer whose bulb is immersed in it stands at $180°$. During this final evaporation one must give it constant attention, for if it is left and the temperature rises above $180°$, not only does the ortho-phosphoric acid become changed partially into pyrophosphoric acid, but it attacks very strongly the material of the dish, and the preparation becomes contaminated with silicic acid. Pour the liquid while still warm into a previously weighed small glass-stoppered bottle, and stopper it tightly. When cool introduce a small crystal of phosphoric acid to induce crystallization of the mass.

NOTE. — If no crystallized phosphoric acid is obtainable the sirupy acid obtained above can be made to crystallize spontaneously if it is placed in a vacuum desiccator over concentrated sulphuric acid and cooled with a freezing mixture.

Questions

1. Write the reaction by which phosphoric acid can be prepared from calcium phosphate.

2. How can phosphoric anhydride, pyrophosphoric acid, and metaphosphoric acid be prepared? Give symbols. Why cannot the anhydride be prepared by heating ortho-phosphoric acid? For what practical purpose is phosphoric anhydride used?

3. Compare the acid strength of phosphoric acid with that of other common acids. Do all three hydrogen ions dissociate with equal readiness?

4. Give the symbols of primary, secondary, and tertiary sodium phosphates. State how the solution of each behaves with litmus.

5. Write the reaction for the precipitation which occurs when magnesium chloride is added to a solution of phosphoric acid or a phosphate, which is made strongly ammoniacal. This precipitate constitutes one of the most important tests for phosphoric acid.

6. Give an example of how phosphorous acid may behave as a reducing agent.

27. ARSENIC ACID $(H_3AsO_4)_2.H_2O$

Arsenic acid in its properties shows a striking similarity to phosphoric acid; and even the method of its preparation is similar, in that use is made of the oxidizing action of nitric acid. Instead of starting with uncombined arsenic, however, use is made of arsenious oxide, As_2O_3, a product which condenses in the flues wherever ores which contain arsenic are roasted. By the nitric acid this is oxidized to the higher oxide, As_2O_5, which, with water, yields arsenic acid, H_3AsO_4. From the salts which arsenic acid forms, it is known to be, like phosphoric acid, a tribasic acid, that is, one which yields three hydrogen ions. By evaporating its solution for a long time on the water bath, crystals of ortho-arsenic acid having the composition H_3AsO_4 can be ob-

tained. By prolonged evaporation at higher temperatures crystals of the composition $H_4As_2O_7$ and $HAsO_3$, respectively, can be obtained. When a solution of arsenic acid is boiled down according to the following directions, a liquid is obtained of almost exactly the composition given by the formula $(H_3AsO_4)_2.H_2O$. This liquid when cooled to $35.5°$ or below can be crystallized to a solid product of the same composition, and this is the most satisfactory form in which to crystallize arsenic acid. It is interesting to note that this liquid can be much supercooled below $35.5°$, but that when once crystallization is induced the temperature immediately rises to this point and remains there until solidification is complete. Likewise when the solid is being melted the temperature will not rise above the melting point, $35.5°$, until the whole mass is liquefied.

Procedure. — Place 50 grams of arsenious oxide in a good-sized casserole ; add 20 cc. of water, and then at the hood add 75 cc. of concentrated nitric acid ; warm occasionally just enough to keep up the action, but do not allow the reaction to become violent, because the heat would drive off the nitric acid. Finally, after red fumes cease to be evolved, evaporate the liquid, holding the casserole in the hand and rotating it all the while, until the residue is just dry. When cool enough add 60 cc. of water, and heat until the residue is completely dissolved.[1] Evaporate the solution by boiling it gently in a small casserole until the temperature has risen to $115°$. Then transfer the liquid to a very narrow beaker or test tube, and boil it carefully with a small flame until the temperature shown by a thermometer inserted

[1] If complete solution does not take place after heating for some minutes, either the oxidation of the arsenious oxide has not been complete or else the residue has been heated too strongly. Test for arsenious acid according to the directions in Experiment 5. If any is found it must be oxidized by the addition of more nitric acid, and the liquid must again be evaporated to dryness.

in the liquid has just risen to 160°. Cool the product to below 35.5°, place it in a weighed sample bottle, and seed it with a small crystal of $(H_3AsO_4)_2.H_2O$, whereupon the whole will slowly crystallize to a solid mass. Stopper the bottle tightly, since arsenic acid takes moisture rapidly from the atmosphere.

Questions

1. Give the reaction of nitric acid upon arsenious oxide.

2. Compare the strength of arsenic acid with that of phosphoric acid; with that of arsenious acid.

3. *Experiment.* — To a solution of arsenic acid (0.1 gram in 10 cc. of water) add magnesium chloride and then ammonia until strongly alkaline. Compare with 5 under Phosphoric Acid.

4. *Experiment.* — Add a little potassium iodide solution to some arsenic acid solution, and warm gently. Is iodine set free? Give the reaction.

Prepare a faintly alkaline solution of arsenious acid as follows: Dissolve a minute quantity of arsenious oxide in not more than 2 or 3 drops of hydrochloric acid; dilute to 10 cc. and add, without heating, a considerable amount of sodium bicarbonate in excess of what is necessary to neutralize the acid. To this solution add, drop by drop, a solution of iodine, and determine if any free iodine disappears. Write the reaction. It is, so far as the state of oxidation of the arsenic is concerned, exactly the reverse of the one preceding. Recall a previous instance in which the direction of a reaction of oxidation and reduction is changed on passing from an acid to an alkaline solution.

5. *Experiment.* — Test for arsenious acid in your preparation: Dissolve a small crystal of the arsenic acid in a few centimeters of water; add sodium bicarbonate until no more effervescence occurs, and then a considerable quantity

in addition. Add to this a solution of iodine, drop by drop. The amount of the latter which is decolorized (if any) corresponds to the amount of arsenious acid which was in the sample.

28 ANTIMONY TRICHLORIDE FROM STIBNITE

(BY–PRODUCT: ANTIMONY OXYCHLORIDE)

Native antimony sulphide (stibnite) dissolves quite readily in hydrochloric acid, yielding antimony trichloride,

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$
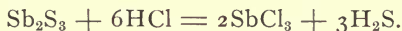
If the solution so obtained is distilled, there pass off at first only steam and hydrochloric acid, later a mixture of hydrochloric acid and antimony trichloride, and finally pure antimony trichloride.

The salt antimony trichloride hydrolyzes with a moderate amount of water, giving a precipitate according to the reactions,

$$SbCl_3 + 2H_2O = SbCl(OH)_2 + 2HCl,$$
$$SbCl(OH)_2 = SbOCl + H_2O;$$
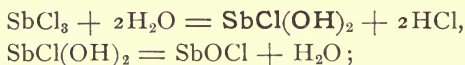
with more water a further hydrolysis takes place:

$$4SbOCl + H_2O = Sb_4O_5Cl_2 + 2HCl.$$
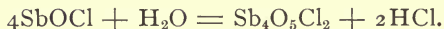
The product obtained in this preparation by mixing the next to the last distillates with a considerable amount of water has the latter composition. This compound, however, if repeatedly boiled with fresh portions of water may be made to undergo complete hydrolysis, leaving finally only Sb_2O_3.

Procedure. — Treat 150 grams of powdered stibnite in an 8-inch dish at the hood with 750 cc. of commercial hydrochloric acid (sp. gr. 1.2); warm the mixture slightly and keep it at 50–70°, with frequent stirring, for 20 minutes

Finally, boil the solution for 5 minutes. Then add 15 cc. more of concentrated hydrochloric acid; filter the solution through asbestos felt (Note 4 (*d*)) which has previously been moistened with hydrochloric acid, and rinse the residue onto the filter with an additional 15 cc. of hydrochloric acid. Evaporate the filtrate in an open dish to 200 cc.; then transfer it to a retort, in the bottom of which is placed, to prevent bumping, about a teaspoonful of small bits cracked from an unglazed porcelain dish. Place the retort on a sand bath and distill, after first covering the bulb of the retort with an asbestos mantle to prevent loss of heat. At first insert the neck of the retort into a liter flask half filled with cold water (to absorb the hydrochloric acid). When a little of the distillate begins to give a precipitate on dropping into a tube of cold water, exchange the receiving flask for a smaller dry one and continue the distillation until a drop of the distillate will solidify when cooled on a watch glass. Save the portion thus obtained for later use and continue distilling, using a wide 6-inch test tube, which has previously been weighed, as a receiving vessel, until the liquid is all driven out of the retort. Stopper the test tube tightly and preserve the preparation in it. If the product thus obtained is not white it should be dissolved in concentrated hydrochloric acid and redistilled.

NOTE. — In case the stibnite used contains a considerable quantity of silicates soluble in acids, there will be left in the retort as the distillation progresses a quantity of gelatinous silicic acid which is liable to interfere with obtaining distinct fractions of the distillate. In such a case distill until the residue in the retort is left dry, but without making the final change in receiving vessels. Then pour all of the distillate containing any of the antimony salt into a fresh retort and distill again, this time separating the fractions.

Antimony Oxychloride. — Pour the portion of the distillate saved from the above procedure into 2 liters of water. Stir, allow to settle, and draw off the clear liquid. Stir up with water once more, let settle, and draw off as much of

the water as possible. Drain the precipitate on a Witt filter, and spread it on an unglazed plate to dry.

Questions

1. *Experiment.* — Prepare a solution of antimony trichloride. How can the formation of a precipitate be avoided? Pass hydrogen sulphide into this solution. What is the precipitate? How could it be converted into a product like stibnite?

2. How would the reactions of phosphorus and arsenic trichlorides with water differ from that of antimony trichloride? Is hydrolysis more or less complete in these cases? Why, then, is there no precipitate?

29. SODIUM SULPHANTIMONATE $Na_3SbS_4.9H_2O$

The oxides of arsenic and antimony, and more particularly the higher oxides, are acidic in nature; thus with basic oxides they will form salts:

$$3Na_2O + As_2O_3 = 2Na_3AsO_3;$$
$$3Na_2O + As_2O_5 = 2Na_3AsO_4.$$
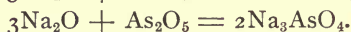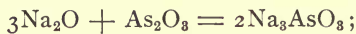
Sulphur, in accord with its similarity to oxygen, can be substituted for the latter in many of its compounds without essentially altering their chemical nature, and the compounds thus obtained have the same nomenclature as the corresponding oxygen compounds, except that the syllable "sulph" or "sulpho" is inserted. Thus sulpho-salts are produced in the same manner as the oxy-salts above:

$$3Na_2S + As_2S_3 = 2Na_3AsS_3;$$
$$3Na_2S + As_2S_5 = 2Na_3AsS_4.$$
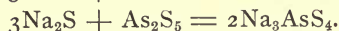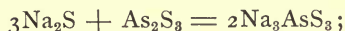
The sulpho-salts of arsenic, antimony, and stannic tin are particularly characteristic of these metals. They are easily produced, and all are soluble. They are stable in neutral

or basic solutions, but are decomposed by acids, because the anions of the salts combine with hydrogen ions to produce the very weak sulpho-acids, which, being unstable, decompose at once into the sulphides of the metals and hydrogen sulphide:

$$6H^+ + 2AsS_3^{---} \rightarrow 2H_3AsS_3 \rightarrow 3H_2S + As_2S_3;$$
$$6H^+ + 2AsS_4^{---} \rightarrow 2H_3AsS_4 \rightarrow 3H_2S + As_2S_5.$$
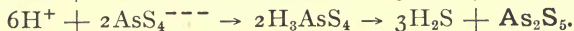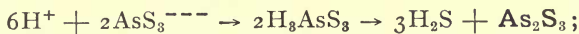
Sodium sulphantimonate can be prepared from stibnite by the combined action of a solution of sodium sulphide and sulphur:

$$2S + Sb_2S_3 \rightarrow Sb_2S_5;$$
$$3Na_2S + Sb_2S_5 \rightarrow 2Na_3SbS_4,$$
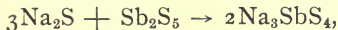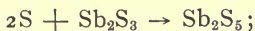
and it crystallizes well with nine molecules of water.

Procedure. — To 50 grams of powdered stibnite, 107 grams of crystallized sodium sulphide ($Na_2S.9H_2O$),[1] and 10 grams of powdered sulphur in a porcelain dish, add 100 cc. of water, bring to a boil, and keep at the boiling temperature for $\frac{1}{4}$ of an hour. Filter and rinse the residue in the dish and on the filter with hot water, bringing up the volume of the solution to 200 cc. While still hot put it away in a covered dish, with a towel placed over it, to crystallize. Drain the crystals; evaporate the mother liquor somewhat to obtain a second crop of crystals. Spread the crystals on a porous plate, and stopper them tightly as soon as dry.

Questions

1. *Experiment.* — Prepare a little precipitated antimonous sulphide. How? Treat this precipitate with a solution of ammonium polysulphide, $(NH_4)_2S_x$. Discuss, with reactions, the nature of the soluble compound produced. Finally, acidify the solution with hydrochloric acid. What is the reaction?

[1] Or use 35 grams of anhydrous sodium sulphide and an additional 72 cc. of water.

30. ANTIMONY PENTASULPHIDE, Sb_2S_5

This compound cannot be prepared directly from the trisulphide and sulphur, because it is decomposed at a temperature below that at which the latter substances would react. As has just been seen, however, the higher sulpho-salt of antimony can be readily prepared in the wet way; and this, on decomposition with a dilute acid, yields antimony pentasulphide. This substance is much used in vulcanizing rubber.

Procedure. — Dissolve 40 grams of the sodium sulphantimonate obtained in the last preparation, and dilute with 1 liter of cold water. Mix 15 cc. of concentrated sulphuric acid with 350 cc. of water, cool, and place in a 2-liter, or, better, a 3 or 4-liter common bottle. To this add slowly, and with constant stirring, the solution prepared above. Fill the bottle with water and stir thoroughly. Let the precipitate settle, draw off the liquid, and wash by decantation until the wash water no longer gives, with barium chloride, the test for a sulphate. After the last washing let settle for some time, draw off as much as possible of the clear liquid, and transfer the slime to a large filter (Note 4 (*c*); do not omit to reënforce the point of the filter) to drain for 12 hours or longer. Without removing the pasty antimony sulphide from the filter, open out the latter on an unglazed plate, and leave it on a shelf above the steam table where the temperature does not rise above 50°. When the product is completely dry, detach the hardened lumps from the paper and pulverize them in a mortar.

Questions

1. Write all the reactions involved in the preparation of antimony pentasulphide from stibnite.

31. METALLIC ANTIMONY

This metal is obtained on a commercial scale both by reducing antimony oxide with carbon and by reducing antimony sulphide by means of metallic iron. The latter method possesses the advantage that antimony sulphide, a natural product, is used directly and does not need to be first converted into the oxide. The iron sulphide formed by this method is fusible and forms a slag; but the slag is made more fusible by the admixture of sodium sulphate as directed, and thus the globules of melted antimony are allowed to sink more easily to the bottom of the crucible and form a metallic regulus. The slag furthermore covers the surface of the metal and hinders its volatilization and oxidation.

Procedure. — Mix 100 grams of stibnite with 42 grams of iron filings, 10 grams of anhydrous sodium sulphate, and 2 grams of powdered charcoal, and place the mixture in a clay crucible. Cover the crucible tightly, and heat it in the gas furnace for one hour at a bright red heat. The temperature should not be high enough to volatilize the antimony, which would in that case escape as a white smoke consisting of antimony oxide, yet the slag of iron sulphide must be completely softened, although it should not melt to a thin liquid. After about half an hour test the conditions by removing the cover a moment and stirring the slag with an iron rod to see whether it is in the proper semi-fluid condition. After the reaction is complete, allow the crucible to cool, break it and separate the regulus of antimony from the slag.

Questions

1. *Experiment.* — Warm a piece of metallic antimony with hydrochloric acid. Where does antimony stand in the electromotive series?

2. *Experiment.* — Warm a little powdered antimony with nitric acid in a casserole. What is the product? Compare it with the product obtained by treating tin in the same manner.

32. BISMUTH BASIC NITRATE (BISMUTH SUBNITRATE)

Although bismuth is the most strongly metallic element of the fifth group, yet its salts in aqueous solution undergo partial hydrolysis very readily. In presence of a considerable amount of free acid, the Bi^{+++}-ion is capable of existence in solution; but with decreasing quantities of acid the tendency of water to produce hydrolysis increases, and the basic salt of bismuth, which is only slightly soluble, separates:

$$Bi^{+++} + 3NO_3^- + 2H_2O \rightleftharpoons Bi{\overset{\displaystyle OH}{\underset{\displaystyle NO_3}{-OH}}} + 2H^+ + 2NO_3^-.$$
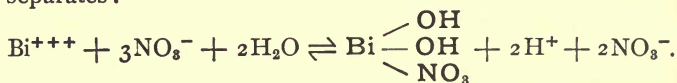
On pouring a solution of bismuth nitrate into a considerable quantity of cold water the basic nitrate, according to the above formula, is precipitated. This salt, however, is not stable in contact with a solution which does not contain nitric acid of a concentration of at least about $\frac{1}{2}$ molal, but slowly changes over into some other more basic nitrate, and if washed repeatedly with pure water will finally go over completely into the hydroxide:

$$Bi{\overset{\displaystyle OH}{\underset{\displaystyle NO_3}{-OH}}} + H_2O \rightleftharpoons Bi{\overset{\displaystyle OH}{\underset{\displaystyle OH}{-OH}}} + H^+ + NO_3^-.$$
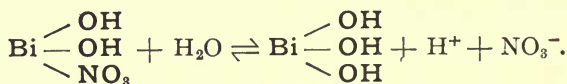
Under the conditions given in the following procedure, this production of a more basic salt will occur if the precipitate is allowed to stand in contact with the solution for a considerable time; hence the directions to filter at once.

The basic nitrate is by no means completely insoluble in water, and the filtrate contains considerable quantities of bismuth, which can be conveniently saved as oxide by precipitating with sodium carbonate.

Procedure. — Dissolve without heating 40 grams of crystallized bismuth nitrate, $Bi(NO_3)_3.5H_2O$, in 10 cc. of nitric acid (sp. gr. 1.2) and 20 cc. of water. Pour this into 2 liters of cold water and stir thoroughly for a few minutes. Let the precipitate settle completely, and as soon as this has occurred draw off and save the supernatant liquor; drain the precipitate on a suction filter, and wash it quickly with about 20 cc. of water. Dry the precipitate at the steam table, and preserve it as a powder.

Bismuth Oxide. — Combine all the liquors from the foregoing; add sodium carbonate until alkaline to litmus; let settle, and draw off the supernatant liquor; boil the remaining suspension after adding to it about 20 grams more of sodium carbonate. Then wash the precipitate twice by decantation, drain on a suction filter, and wash with two or three portions of water. Dry and preserve.

Questions

1. In accordance with the above directions, sodium carbonate is used to precipitate bismuth hydroxide. Why should not the precipitate be bismuth carbonate?

2. If this precipitate is not finally boiled with an excess of sodium carbonate, it is likely to contain a certain amount of basic nitrate. Explain why this should be so and why the boiling will convert it completely into the hydroxide.

GENERAL QUESTIONS. V

ELEMENTS OF THE FIFTH GROUP OF THE PERIODIC SYSTEM

Experiments

(The results observed are to be recorded in the laboratory note-book at the time the experiments are performed.)

1.   Boil about $\frac{1}{2}$ gram of powdered metallic arsenic with nitric acid (1.2) until the metal is entirely dissolved.   Evaporate the solution just to dryness by heating it over a free flame in a casserole while holding the latter in the hand and rotating its contents.   In this way all the unused nitric acid is expelled.   When cool add 10 cc. of water and warm until the arsenic acid has all dissolved.   Prove that the solution contains an acid (*i. e.*, more than an accidental trace of nitric acid, which might not have been completely expelled and might be sufficient to redden litmus).

Boil about $\frac{1}{2}$ gram of powdered antimony with nitric acid (1.2).   What is the character of the product formed?

Treat $\frac{1}{2}$ gram of powdered bismuth in the same manner. Evaporate the solution so obtained to a very small volume (about 1 cc.) to remove most of the surplus nitric acid. Then pour the solution into 50 cc. or more of cold water.

2.   Pass hydrogen sulphide into hot dilute solutions of arsenic, antimony, and bismuth trichlorides in separate test tubes.   Note the color of the precipitates.   Collect each precipitate on a filter and treat it with warm ammonium polysulphide (ammonium sulphide in which more sulphur is dissolved).   Lastly, acidify with hydrochloric acid each of the solutions so obtained.

Questions

1.   Of Group V only those elements falling in the right-hand sub-column need especial consideration, namely, nitrogen, phosphorus, arsenic, antimony, and bismuth. In this series we pass by a very

perfect gradation from nitrogen, a pronounced non-metal, to bismuth, a quite pronounced metal.

State in each case whether the nitrate or sulphate of trivalent phosphorus, arsenic, antimony, or bismuth can be prepared, and if so whether it can be dissolved in water without suffering complete hydrolysis (see Experiment 1). How does the basic nature of the trioxide change in the series, phosphorus to bismuth? Can nitrates or sulphates of any of these elements in their pentavalent condition be prepared? For any one of the elements, which is the more strongly basic in nature, the trioxide or the pentoxide? Which is the more strongly acidic? Give the symbol of the most common acid, if one exists, which is derived from the pentoxide of each of these elements. How does the acidic nature of the pentoxide change in passing from nitrogen to bismuth?

2. Name the simplest hydrogen compound of each of the first four elements. Compare the stability of these hydrides when heated. Compare any ability they may possess to unite with water to form bases, and with acids to form salts.

3. Write the equations for the reaction of nitric acid with phosphorus, arsenic, antimony, and bismuth, respectively (see Experiment 1).

4. How do the trisulphides of arsenic and antimony behave when treated with a solution of ammonium sulphide, $(NH_4)_2S$? With a solution of ammonium polysulphide, $(NH_4)_2S.S_x$? How does the solution obtained with ammonium polysulphide behave when it is acidified? Give equations for all the reactions. (See Experiment 2.)

What is the relation between sulpho- and oxy-acids? Show, for example, how sodium sulpharsenate is derived from two simple sulphides, and sodium arsenate from the corresponding oxides.

CHAPTER VI

HEAVY METALS OF THE SIXTH, SEVENTH, AND EIGHTH GROUPS OF THE PERIODIC SYSTEM

By turning to the Periodic Table of the elements it is observed that chromium, manganese, iron, cobalt, and nickel, and following these copper and zinc, come in the middle portion of the long period that begins with potassium and ends with bromine. The seven elements mentioned possess high specific gravities and all come under the classification of *heavy metals*. In certain of their compounds they are extremely similar to one another; in other of their properties they are very dissimilar and exhibit the chemical characteristics of the respective groups to which they belong.

The heavy metals occupying a corresponding position in the middle of the next long period are molybdenum, an unknown element which should come below manganese, ruthenium, rhodium, palladium, silver, and cadmium. In the middle of the next long period come tungsten, another unknown element which should resemble manganese, osmium, iridium, platinum, gold, and mercury. In the last long period, of which there is at best only a fragmentary indication, the only representative of this class of heavy metals is uranium.

In the sixth group, chromium, molybdenum, tungsten, and uranium constitute Family A. In their trioxides they show the characteristic valence of the sixth group and resemble in properties the non-metals of Family B, of which sulphur is the type. In their lower oxides they show none

of the group characteristics, but show the general base-forming properties of the heavy metals.

In the seventh group, manganese, the only known representative of Family A, resembles the halogens in its heptoxide, Mn_2O_7; in its lower oxides it shows no resemblance to the halogens, but does show properties similar to those of other heavy metals when they are in the same state of oxidation; in its lowest oxide, MnO, it is distinctly a base-forming element.

In the eighth group, each position instead of being filled by a single element is occupied by a group of three elements. Thus there appear in triads: iron, cobalt, and nickel; ruthenium, rhodium, and palladium; and osmium, iridium, and platinum. In this group there is no subdivision into A and B Families, but all of the members are heavy metals. The Zero Group, which comprises the inert gases, helium, neon, argon, krypton, and xenon, may be regarded as bearing the same relation to Group VIII as is shown in the other groups between the A and B Families. If this view is a correct one, the divergence in properties between the families is in this case at a maximum.

Of the heavy metals discussed above, the only ones that are of frequent occurrence and that are to receive detailed treatment in this chapter are chromium, manganese, and iron.

The most important source of chromium is the mineral chromite, $FeO.Cr_2O_3$ or $Fe(CrO_2)_2$. This substance, as indicated by the formula, may be regarded as a mixture of ferrous oxide and chromic oxide, or as a salt, chromite of iron, in which ferrous oxide is the basic constituent and chromic oxide the acidic. Chromite is a difficult material to decompose, and the ordinary method by which this is accomplished is by treatment at a high temperature with an alkali and an oxidizing agent. By this treatment the iron of the chromite is converted to the ferric condition (Fe_2O_3), and the chromium is oxidized to the hexavalent condition (CrO_3), at the same time combining with the alkali to form a chromate (for example, K_2CrO_4).

In the commercial method for manufacturing chromates, atmospheric oxygen is utilized as the oxidizing agent. The chromite is mixed with potassium carbonate and calcium carbonate, the latter to give porosity, and then heated for a considerable time in a furnace with free access of air. The chromium trioxide, CrO_3, produced by the oxidation reacts with the potassium carbonate, displacing carbon dioxide and giving potassium chromate, K_2CrO_4. After cooling, the contents of the furnace are treated with a solution of sodium sulphate; the potassium chromate dissolves, the iron oxide is insoluble, and the calcium oxide (from heating the carbonate) reacts with the sodium sulphate to form insoluble calcium sulphate. From the solution potassium chromate could be crystallized but for the fact that it is very soluble in water and could not be separated thus from other salts in the solution. Potassium bichromate, however, is much less soluble, and

if this is formed by adding a sufficient amount of sulphuric acid,

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O,$$

it can be obtained pure by crystallization.

On account of the difficulty of carrying out the above process on a laboratory scale, the following less economical procedure is given in which the mineral is heated with considerably more than the quantity of potassium carbonate theoretically required, in order to give a more liquid melt, and with potassium nitrate for the oxidizing agent. The solution obtained by extracting this melt with water contains so much potassium carbonate that it would be very difficult to separate the also very soluble potassium chromate from it by crystallization. If, however, acetic acid is added until the solution reacts slightly acid, the potassium carbonate is converted into the very soluble acetate, and the chromate is changed to the only moderately soluble potassium bichromate which, especially in the presence of the large amount of the other salt with the K^+-ion in common, can be very readily crystallized out.

A saturated solution contains for each 100 grams of water the given number of grams of the anhydrous salt.

Temperature	0°	10°	20°	30°	40°	50°	70°	100°
K_2CrO_4	59	61	63	65	67	69	73	79
$K_2Cr_2O_7$	5	7	12	20	26	35	55	88

Procedure. — Mix 40 grams of finely powdered chromite [1] with 100 grams of potassium carbonate and 30 grams of

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[1] Unless an ore can be obtained which approximates the composition of the pure mineral, $FeO.Cr_2O_3$, it would prove more satisfactory to take 27 grams of pure chromic oxide, Cr_2O_3, instead of 40 grams of chromite.

potassium nitrate. Place the mixture in a cast-iron crucible, which it must on no account fill more than two-thirds full, else when melted it will run over. Heat in a gas furnace to a white heat (but using care not to reach the very highest heat, which might melt the crucible) until the melted charge has ceased to effervesce. Pour the molten mass out onto a dry[1] iron plate. When cool crack it up and dissolve it, together with what still adheres to the crucible, in boiling water. Filter the solution, and extract the residue with a little more boiling water and pour through the same filter. Add glacial acetic acid (cautiously) to the filtrate until it has become acid. Boil down the solution to 300 cc., or to even a less volume if no solid salt begins to separate. Add 25 cc. more of glacial acetic acid, let stand for some time, and finally cool to 0° before separating the crystal meal of potassium bichromate from the mother liquor. Purify the product by recrystallization.

Questions

1. Mention at least three oxidizing agents which might have been used instead of potassium nitrate in this preparation.

2. How might the oxidation of chromic hydroxide, $Cr(OH)_3$, be accomplished in the wet way? *Experiment.* — To 5 cc. of a cold solution of a chromic salt add about 1 gram of sodium peroxide, agitate for a few moments, and then warm until effervescence ceases. Formulate the equations for the intermediate reactions in such a way as to show the state of oxidation of chromium in each compound involved, and then add the separate equations to give one for the complete reaction.

3. *Experiment.* — To a solution of potassium bichro-

[1] See footnote 2, page 60.

mate add potassium carbonate until no more effervescence occurs. Observe and explain any change in color. To a solution of potassium chromate add an acid and observe as before. Explain fully the relation between chromates and bichromates.

34. POTASSIUM CHROMATE FROM POTASSIUM BICHROMATE

Dissolve 50 grams of potassium bichromate in water and add the calculated amount of potassium carbonate dissolved in water. The color should just change to clear yellow, and no trace should be left of the reddish hue characteristic of the bichromate. Crystallize the product from the solution (see solubility table on page 120).

Answer the questions given under Potassium Bichromate.

35. CHROMIC ANHYDRIDE, CrO_8

When a chromate or a bichromate is treated with a strong acid, chromic acid is formed in the solution. The affinity of chromic anhydride for water is far less than that of sulphuric anhydride for water; and chromic acid, therefore, instead of existing in solution entirely in the form H_2CrO_4, is broken down to a great extent into $H_2Cr_2O_7$ (*i.e.*, $H_2O.2CrO_3$) and even to CrO_8. Especially in the presence of a large amount of sulphuric acid, the last form is produced so freely that it crystallizes out in the shape of red needles.

Commercially, chromic anhydride is most often prepared by the action of sulphuric acid on potassium bichromate. Potassium acid sulphate is first crystallized from the mixture and after that the chromic anhydride; but a good deal of care is necessary to obtain the product uncontaminated with

potassium salt.   When, however, lead chromate is used as
the source of the chromic acid, the lead can be completely
removed, since with sulphuric acid the extremely insoluble
lead sulphate is formed.   The remaining solution then con-
tains nothing but chromic acid and an excess of sulphuric
acid.   The chromic anhydride can then be crystallized out,
it being least soluble in a mixture containing in the neigh-
borhood of 75 per cent. of sulphuric acid.

Procedure. — Lead Chromate.   Dissolve 100 grams of
lead acetate in 1 liter of water, and add a few drops of
acetic acid if necessary to clear up any turbidity.   Dissolve
39 grams of potassium bichromate in 1 liter of water, and
add this solution to the first, while stirring.   Wash the pre-
cipitate by decantation until less than 0.5 per cent. of the
soluble salt remains (Note 5 (*b*) on page 13); then collect
the lead chromate on an ordinary filter (Note 4 (*c*)), and after
draining dry it thoroughly.

Chromic Anhydride. — Take the lead chromate prepared
above (or 100 grams of a commercial sample), reduce all
lumps to a fine powder, add 200 grams of concentrated sul-
phuric acid (111 cc.), and stir the mixture with a pestle until
a perfectly smooth paste is produced.   Allow the mixture to
digest 24 hours in a warm place, as on the shelf above the
steam table.   Dilute to a liter with water, and filter the solu-
tion through asbestos felt (Note 4 (*d*) on page 10).   Wash
the lead sulphate until it is nearly or quite white, separate
it from the asbestos as completely as possible, and preserve
it as a by-product.   Evaporate the filtrate in a porcelain
dish until crystals of chromic anhydride begin to form a
scum on the surface of the liquid.   Let the solution cool
slowly; then collect the crystals in a funnel in which a per-
forated plate or a glass marble is placed, and drain out all
the liquid with suction.   Cover the funnel with a watch
glass while evaporating the liquor to obtain a second crop

of crystals. Collect this crop in the same funnel together with the first crop, and wash the product twice with concentrated nitric acid to remove the sulphuric acid adhering. Use sufficient nitric acid each time to just wet the entire mass of crystals, and then drain it off as thoroughly as possible with the suction (Note 5 (*a*) on page 12). Finally, drive off the nitric acid by heating the crystals very cautiously in a small porcelain dish placed on a sand bath. Keep turning over the mass of crystals with a glass spatula to avoid heating the lower layer too strongly. Chromic anhydride melts at 192°, and care must be taken to avoid reaching this temperature. When the crystals appear dry and no more white vapor can be detected on breathing across them, preserve them in a glass-stoppered bottle.

Questions

1. When chromic anhydride is dissolved in water, what components are produced in the solution? What salt is precipitated if lead acetate or barium acetate is added to this solution? Why is it not the bichromate which is obtained?

2. *Experiment.* — Heat a little chromic anhydride strongly on a bit of porcelain. What color change occurs? (The color of the product can be better observed if a particle is pulverized in a white mortar.) Is the product soluble in water? In hydrochloric acid? What relation does it bear to the mineral chromite?

36. CHROMIC ALUM

The preparation of potassium bichromate illustrated how chromic oxide, Cr_2O_3, as it exists in nature as a constituent of the mineral chromite, can be oxidized to a chromate in which chromium exists as CrO_3. For the preparation of

chromic alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, it might seem as if chromite should yield chromic sulphate directly on treatment with sulphuric acid. This is, however, impossible, because the natural material is, as already stated, very resistant to the action of acids. It yields only to the action of powerful oxidizing agents, which convert it into a chromate, and therefore potassium, or sodium, bichromates are always the products made directly from the mineral, and these serve as the materials from which other compounds of chromium are prepared. To make chromic alum from potassium bichromate it is necessary to reduce the chromium to the same state of oxidation in which it originally existed in the mineral, and to add sufficient sulphuric acid to form the sulphates of potassium and chromium. Alcohol may be used as the reducing agent, it being itself oxidized to aldehyde, a body whose presence is made very evident by its penetrating odor.

Chromic alum is isomorphous with common alum and can easily be obtained in large and beautiful deep purple crystals. Care must, however, be exercised not to allow the temperature of its solution to rise above $50°$ during the preparation, for when heated beyond this point it undergoes a change into a green noncrystallizable body. This green body is not stable at the ordinary temperature, and after cooling it will change slowly back into the ordinary crystallizable chromic alum ; but so slowly, however, that if once it is formed the preparation is practically spoiled.

At $25°$, 24 grams of $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ will dissolve in 100 grams of water, and the solubility increases very rapidly with the temperature.

Procedure. — Pulverize 100 grams of potassium bichromate, and cover it in an 8-inch evaporating dish with 400 cc. of water. Add 78 cc. of concentrated sulphuric acid, and stir until the bichromate is all dissolved. Adding

the sulphuric acid should produce enough heat to dissolve
the bichromate, but if it is necessary heat the mixture a
little more.   Be sure that the last trace of solid is dissolved.
Allow the solution to cool to 40°; then add alcohol, a drop
at a time, while stirring constantly with the stem of a ther-
mometer until the temperature commences to rise.   Then
place the dish in a pan of ice and water and add alcohol,
65 cc. in all, at first very slowly, endeavoring to keep the
temperature between 35° and 40°, and finally more rapidly.
Keep the temperature at all times well below 50°; and if it
should start to rise suddenly, due to too large an addition
of alcohol, and get as high as 50°, drop a piece of ice
directly into the solution.   Finally, let the solution cool
completely in the bath of ice water, or, still better, let it
stand over night.   Collect the crystal meal on a Witt filter
and suck it free from liquid.   Recrystallize so as to obtain
large, well-shaped crystals, following a similar procedure and
observing the same precautions as with common alum (see
page 54).   A saturated solution of this salt should be pre-
pared at 35°.   After freeing it of any undissolved particles
of the crystal meal, warm it to 40°, and set it to crystallize,
with the addition of about ten very small crystals to serve
as nuclei.   Dry with filter paper the crystals so obtained,
and stopper them at once in a bottle, since they are quite
efflorescent.

Questions

1.   Formulate the equations for the separate reactions
involved in the reduction of the bichromate, in such a way
as to show the changes occurring in the state of oxida-
tion of the chromium; the alcohol, C_2H_6O, is oxidized to
aldehyde, C_2H_4O.

2.   Sulphur dioxide might serve as the reducing agent.
Give equations for the partial and complete reactions.

3. Dissolve $\frac{1}{2}$ gram of potassium bichromate in 10 cc. of water and add 10 cc. of dilute sulphuric acid. Heat to boiling, and pass in hydrogen sulphide until the color is changed completely to green. To what is the green color due? What is the precipitate? Formulate equations also for this reaction.

37. CHROMIUM METAL BY THE GOLDSCHMIDT PROCESS

The readiest method of obtaining the metal chromium from its oxide, and one which yields it in a high state of purity, is the so-called Goldschmidt Process, in which use is made of metallic aluminum as the reducing agent according to the reaction,

$$2Al + Cr_2O_3 = Al_2O_3 + 2Cr.$$
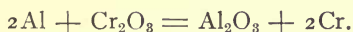
The heat produced by the oxidation of aluminum is so great that it is sufficient to effect the decomposition of the chromic oxide with still enough surplus heat to produce a temperature high enough to melt the metallic chromium. It is evident that before this reaction can be made to progress spontaneously a sufficient temperature must be developed to decompose the chromium oxide. This necessary temperature is a good deal higher than that of a Bunsen flame or of a common furnace, but can be obtained by use of the fuse powder described below. When once started in this way the reaction itself produces a temperature high enough to insure its continuance.

Carried out on the small scale of a laboratory preparation, the heat produced is not quite sufficient to melt the metal and slag so thoroughly that the metal can settle out to form a compact regulus at the bottom of the crucible. By adding a small amount of potassium bichromate to the

charge, however, the reaction becomes more energetic, owing to the more available supply of oxygen.

Procedure. — Heat some powdered chromic oxide in an iron pan over a Bunsen burner. Melt some potassium bichromate in a clean iron pan and pulverize it in a mortar after it has again solidified. It is necessary for the materials used to be entirely free from moisture. Mix 210 grams of the ignited chromic oxide, 60 grams of the fused potassium bichromate, and 96 grams of granulated aluminum (not the powder which is used for a pigment), pack the mixture closely into a clay crucible, and embed the latter in a pail of sand. Make a hole about 4 cm. deep in the middle of the charge, and fill it with about 10 grams of a fuse powder made from 10 parts of barium peroxide and 1 part of granulated aluminum. Insert a strip of magnesium ribbon into the fuse powder. Place the whole under the hood at a distance from any woodwork, and start the reaction by igniting the end of the magnesium ribbon with a Bunsen flame. It is advisable for the operator to wear colored glasses while watching the reaction, and to keep at a little distance to be out of the way of flying sparks. When the crucible has cooled, break it and separate the regulus of metallic chromium from the slag of fused aluminum oxide.

38. MANGANESE CHLORIDE FROM WASTE MANGANESE LIQUORS

The waste liquors left after the generation of chlorine from manganese dioxide and hydrochloric acid contain principally manganous chloride. Besides this, however, there is always some free acid and almost always a considerable amount of ferric chloride present. The greater part of the free acid can be removed by evaporating the

solution until a pasty mass is left which will solidify on cooling. The iron can be removed from the solution of this residue in virtue of the ease with which ferric salts hydrolyze. The nearly neutral solution is treated with suspended manganous carbonate (obtained by treating a part of the solution itself with a soluble carbonate). Ferric chloride hydrolyzes according to the reversible reaction, $FeCl_3 + 3H_2O \rightleftharpoons 3HCl + Fe(OH)_3$. In the ·presence of manganous carbonate the small amount of free acid thus formed is continuously used up according to the reaction, $MnCO_3 + 2HCl \rightarrow MnCl_2 + H_2O + CO_2$. Thus the reaction of hydrolysis is enabled to run to completion. The remaining solution, which is almost absolutely neutral and entirely free from iron salts, yields crystallized manganous chloride, $MnCl_2.4H_2O$, upon evaporation.

$Procedure.$ — Boil 500 cc. of waste manganese liquor in a 6-inch evaporating dish under the hood until the residue becomes pasty. After a scum begins to form on the surface of the liquid, there is danger of spattering and the mixture should be stirred with a glass rod until it becomes semi-solid. Heat the residue to boiling with 1,000 cc. of water; without filtering the solution obtained, take one-tenth of it, dilute this portion to 1,000 cc., and add a solution of sodium carbonate to it until all of the manganese is precipitated as carbonate (test for complete precipitation). Transfer the precipitate to a tall, common bottle and wash it by decantation at least four times. Add the slime of manganous carbonate to the remaining nine-tenths of the manganous chloride solution, and boil the mixture in a casserole until a few drops of the filtered liquid give no red color when tested with potassium sulphocyanate. Filter the solution and evaporate it in an 8-inch dish until a crystal scum forms on blowing across the surface. Then allow the solution to cool slowly and crystallize, leaving it for at least 12 hours

uncovered in a place protected from dust Collect the crystals and evaporate the mother liquor to obtain further crops of crystals until practically all of the salt has crystallized.[1] Spread the light pink crystals on an unglazed plate to dry.

Questions

1. Explain the purpose of the test with potassium sulphocyanate.

2. Explain the action of manganese dioxide in the generation of chlorine gas from hydrochloric acid. In what state of oxidation does manganese exist in the salt manganous chloride?

3. If iron were in the ferrous condition, it would not be removed from the solution by the above procedure. Explain why iron is necessarily in the ferric condition in the liquors used.

4. *Experiment.* — Dissolve a small grain of manganous chloride in a half test tube of water. Test the solution with hydrogen sulphide; then add a few drops of ammonia, and if necessary pass in a little more hydrogen sulphide. Then add acetic acid (a weak acid) until the solution is again faintly acid. Does the manganous sulphide dissolve? Compare the solubility of manganous sulphide with that of copper sulphide; of zinc sulphide.

5. In testing for the complete precipitation of iron from the manganese chloride solution, what would be the effect observed on adding ammonium sulphide (*a*) before, and (*b*) after, all the iron has been precipitated?

[1] The crystals of manganous chloride are deliquescent when the temperature is low and the atmosphere charged with moisture. If the product cannot be obtained satisfactorily by the above directions, carry out the crystallization and drying in a place at a slightly elevated temperature, 25–30°; or cool the saturated hot solution rapidly by stirring or shaking, and dry the crystal meal so obtained by rinsing it with alcohol and then letting the latter evaporate rapidly.

6. Explain how facts involved in the foregoing prepa-
ration show that $Mn(OH)_2$ is more strongly basic than
$Fe(OH)_3$.

39. POTASSIUM PERMANGANATE FROM
MANGANESE DIOXIDE

Although manganese dioxide is a powerful oxidizing
agent, it is nevertheless capable of being itself oxidized
when it is fused with a basic flux. The trioxide of manga-
nese is acidic in nature and combines with the base to form
a salt. Thus it is evident that the presence of a base favors
the oxidation.

The dioxide of manganese is neither strongly basic nor
acidic in nature and shows no marked tendency to form salts.
The monoxide is distinctly basic and the trioxide is distinctly
acidic, so that the former forms salts with acids and the
latter with bases. It follows, therefore, that in the presence
of acids the dioxide has a tendency to produce salts of man-
ganous oxide whereby an atom of oxygen is set free (see
No. 38, Manganous Chloride), and that in the presence of
bases manganese dioxide has a tendency to take on another
atom of oxygen in order to produce a salt of the trioxide.

Thus when manganese dioxide is fused with potassium
hydroxide and an oxidizing agent, the salt potassium man-
ganate is formed. This salt is soluble in water and is fairly
stable so long as a considerable excess of potassium hydrox-
ide is present; but in presence of an acid — even so weak
a one as carbonic acid — the manganate decomposes spon-
taneously, two-thirds being oxidized to permanganate at
the expense of the other one-third, which is reduced again
to manganese dioxide:

$$3H_2MnO_4 \rightarrow 2HMnO_4 + MnO_2 + 2H_2O.$$
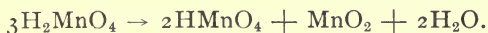
The permanganate (or permanganic acid) corresponds to

the heptoxide of manganese, Mn_2O_7, which is the most strongly acid-forming of the oxides of manganese. Permanganic acid is a strong and very soluble acid, it being of approximately the same acid strength as nitric or hydrochloric acids. It is in addition a very powerful oxidizing agent.

Procedure. — Place 50 grams of potassium hydroxide and 25 grams of potassium chlorate in an 8 cm. sheet iron crucible. Heat the mixture carefully until it is just melted. Meantime grind 50 grams of pyrolusite to as fine a powder as possible (the finer it is ground, the more successful the preparation). Remove the flame from under the crucible and add the pyrolusite, a little at a time, stirring vigorously with an iron spatula (an old file with a wooden handle) all the while.[1] After all is added, place a small flame below the crucible, and keep stirring the charge. Gradually increase the strength of the flame, and stir continuously until the mass stiffens completely. Then cover the crucible and heat it 5 minutes longer at a dull red heat. When the mass has cooled, place crucible and all in 1 liter of water in an 8-inch porcelain dish. After the solid has entirely disintegrated, remove the crucible and rinse it off with a little water from the wash bottle. Boil the solution in the dish, and at the same time pass in carbon dioxide generated from marble and hydrochloric acid until the green color of the manganate has entirely changed to the violet-red color of the permanganate. Test the color by touching a drop of the solution on a stirring rod to a piece of filter paper. If the spot is violet with no trace of green and only a fleck of brown manganese dioxide in the center, the change to

[1] Since the charge in the crucible effervesces and spatters particles of melted salt, great care should be taken to keep the eyes at a safe distance. The hand holding the stirrer should be protected with a thick glove or with a towel, and with the other hand the crucible should be held firmly by means of long iron tongs.

permanganate is complete. Remove the lamp; let the sludge settle in the dish for 5 minutes; then pour the solution through an asbestos filter (see Note 4 (*d*) on page 10), being careful to avoid stirring up the sludge until the very last, since the slimy precipitate of manganese dioxide would so clog the filter as to nearly stop the flow. Lastly, with the aid of a jet of water from the wash bottle, transfer all the sludge to the filter and drain it free from liquid. Evaporate the solution in a clean dish to a volume of 300 cc. Let it settle a moment and filter it through asbestos as before. Pour the filtrate into a 6-inch dish, and allow it to cool slowly in a place protected from the dust. When cold, collect the crystals of potassium permanganate on a perforated plate placed loosely in a filter funnel. Evaporate the mother liquor to 100 cc., filter it through asbestos, and obtain a second crop of crystals. Discard the remaining liquid, since it cannot contain more than about 6 grams of potassium permanganate and to evaporate it further would cause potassium chloride also to crystallize out. Weigh all the crystals, dissolve them in eight times their weight of water (to give a saturated solution at about 40°), filter the solution through asbestos at near the boiling temperature, and let it cool slowly and crystallize in a small porcelain dish covered with a watch glass. Recover another crop of crystals in the same way from the mother liquor, after evaporating it to a volume of 60 cc. Allow the crystals to dry on a clean unglazed plate.

Questions

1. Name and give the symbols of all the oxides of manganese.

2. From which oxide is K_2MnO_4 derived? $KMnO_4$?

3. Write the reactions involved in the above preparation.

4. How could $KMnO_4$ be converted back into K_2MnO_4? Reaction?

5. Does it frequently happen that, with an element which can exist in several states of oxidation, a compound derived from one oxide is stable in an alkaline solution but unstable in an acid solution, while in the latter solution the compound derived from another oxide is the stable one? What other preparation besides the present one illustrates this point?

40. MANGANESE METAL BY THE GOLDSCHMIDT PROCESS

The principle of the production of manganese by this process is exactly the same as that of the production of chromium in Exercise 33. On account of the violence of the reaction between the oxide of manganese and aluminum it is not advisable to ignite the whole charge at once in the crucible; yet on account of the high melting point of manganese a considerable quantity of charge must be used in order to produce heat enough to obtain the metal melted together in a uniform lump, instead of distributed in small globules throughout the mass of the slag. Before mixing up the charge, the pyrolusite which is used must be first heated by itself in order to drive off any water which it may contain and to convert it to the lower oxide, Mn_2O_3.

Procedure. — Place 1 kilogram of finely powdered pyrolusite in a Hessian crucible and heat to a bright heat in a gas furnace. To prepare the charge, mix 750 grams of this material, when it is cooled sufficiently, with 250 grams of granulated aluminum. Heat the empty crucible again in the furnace, and while still hot place it in a pail of sand, as in the preparation of chromium. Place about 20 grams of the charge in the bottom of the hot crucible. Put on colored glasses and a heavy glove; start the reaction with a little fuse powder and a magnesium ribbon (see

Chromium), and then add fresh portions of the charge rapidly but without allowing the reaction to become too violent. When the crucible has cooled, break it, and separate the regulus of metallic manganese from the slag of fused aluminum oxide.

Questions

1. If pyrolusite containing water were used without previous heating, what disadvantage would result during the process?

2. What economy of materials is effected by converting the manganese dioxide into the lower oxide?

41. FERROUS AMMONIUM SULPHATE
$FeSO_4.(NH_4)_2SO_4.6H_2O$
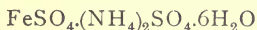
Corresponding to the two most important oxides of iron, FeO and Fe_2O_3, the two sulphates, $FeSO_4$ and $Fe_2(SO_4)_3$, can be prepared. By dissolving iron in sulphuric acid a solution of ferrous sulphate is obtained. This, however, is readily oxidizable, slowly even by the oxygen of the air, to the higher sulphate, and ferrous sulphate can only be preserved free from ferric salt when all oxygen is excluded, or when it is kept in contact with an excess of metallic iron in an acidified solution. Dry crystallized ferrous sulphate or green vitriol, $FeSO_4.7H_2O$, can be preserved fairly well without becoming oxidized; but the double ferrous and ammonium sulphate is not only more easily prepared on account of the readiness with which it crystallizes, but it is also much less easily oxidized by contact with the air.

Procedure. — Prepare crystallized ferrous ammonium sulphate from equimolal quantities of crystallized ferrous sulphate and ammonium sulphate, using 70 grams of the former and

33 grams of the latter. In crystallizing the product, observe the solubilities given in the following table, and make use of suggestions given in Note 8, page 15 and under Alum, page 54:

A saturated solution contains for each 100 grams of water the given number of grams of the anhydrous salt.

Temperature	0°	10°	20°	30°	40°	50°	70°	90°
$FeSO_4$	16	21	26	33	44	48	56	43
$(NH_4)_2SO_4$	71	73	75	78	81	84	92	99
$FeSO_4.(NH_4)_2SO_4$	12	17	22	28	33	40	52	. .

Questions

1. Dissolve a little of the preparation in water and test it with potassium ferrocyanide. If the precipitate is white or only a pale blue, of what does it consist? If it is deep blue, what is shown?

42. FERRIC AMMONIUM ALUM

In this preparation ferrous sulphate is converted into ferric sulphate under the oxidizing action of nitric acid in the presence of the amount of sulphuric acid theoretically necessary to form this salt. By the addition of ammonium sulphate the double salt, ferric ammonium sulphate, $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, crystallizes, this being one of the isomorphous series of alums (see Alum).

At 25°, 100 grams of water dissolve 44 grams of the anhydrous or 124 grams of the hydrated ferric ammonium sulphate.

Procedure. — Heat together 100 grams of crystallized ferrous sulphate, 100 cc. of water, and 12 cc. of concentrated sulphuric acid until the salt is dissolved. While the

solution is boiling, add concentrated nitric acid, a little at a time, until the iron is completely oxidized to ferric sul·phate and a few drops of the solution diluted with a few cubic centimeters of water give no blue precipitate with potassium ferricyanide. Evaporate the solution until it is thick and sticky and most of the excess of nitric acid has been driven off. Dissolve this in water, making up to a volume of 125 cc.; heat to boiling and add 25 grams of ammonium sulphate dissolved in 100 cc. of hot water. Allow the solution to cool slowly and crystallize. Collect the crystals in a funnel; wash with a very little water and allow to dry on an unglazed plate. Obtain a second crop of crystals from the mother liquor.

Questions

1. Write the reaction involved in the oxidation of ferrous sulphate as carried out in this preparation.

If an unacidified solution of ferrous sulphate is oxidized by the oxygen of the air, what products are formed?

2. Write the reaction involved in the test for ferrous salt with potassium ferricyanide.

3. *Experiment.* — Prepare a solution of a ferrous salt by dissolving 2 grams of ferrous ammonium sulphate in 20 cc. of water, adding a little dilute sulphuric acid and a piece of iron wire. Test both this solution and a solution of a ferric salt (nitrate or chloride) with potassium ferrocyanide, potassium ferricyanide, and potassium sulphocyanate. Tabulate the results. These constitute the standard tests for ferrous and ferric salts.

GENERAL QUESTIONS. VI

HEAVY METALS OF THE SIXTH, SEVENTH, AND EIGHTH GROUPS OF THE PERIODIC SYSTEM

Experiments

(The results observed are to be recorded in the laboratory note-book at the time the experiments are performed.)

1.   Test the stability of nickel carbonate by heating 1 gram of it gently in a test tube while shaking it in a Bunsen flame.   Test the gas evolved for carbon dioxide ; and compare the action of the remaining solid, when treated with hydrochloric acid, with that of the original carbonate. The carbonates of divalent iron, cobalt, manganese, and chromium are all of approximately the same degree of stability as nickel carbonate, so that this one experiment may be taken as typical of this class of carbonates.

2.   *To Show Whether the Carbonate of a Trivalent Metal Can Exist.* — Dissolve 2 grams of ferric alum in 10 cc. of water (this gives a trivalent iron salt in a solution that contains no free acid).   Add a 10 per cent. sodium carbonate solution slowly until no more action takes place.   What is the gas evolved ?   What is the precipitate ?   In this experiment the ions Fe^{+++} and CO_3^{--} are brought together ; the other ions, Na^+ and SO_4^{--}, could not react together to give any visible effect.   If, therefore, ferric carbonate is stable in contact with water, it will either form a precipitate if it is insoluble, or if it is soluble it will simply stay in solution and no effect will be observable.   The gas given off shows that the carbonate is unstable.   Write the equation for the reaction.   None of the carbonates of the metals of this group, when they are in the trivalent condition, are any more stable than ferric carbonate.   A salt of chromium, such as chromic alum, might be used instead of ferric alum in the above experiment.

3. *Oxidation of a Divalent Oxide.* — Heat $\frac{1}{2}$ gram of cobalt carbonate in an open porcelain dish, holding the dish with tongs and keeping it rotating in the flame, but not allowing the porcelain to even approach a visible red heat. Heat until the color of the cobalt carbonate has completely changed. Like nickel carbonate, cobalt carbonate is decomposed by heat into cobaltous oxide, CoO, and carbon dioxide. If the cobaltous oxide is readily oxidized by the oxygen of the air, it may at once be changed into Co_2O_8 or Co_3O_4. To test for this, treat a little of the product with hydrochloric acid in a test tube. From CoO the salt $CoCl_2$ would be obtained. From Co_2O_8 or Co_3O_4 the same salt, $CoCl_2$, would be obtained — not $CoCl_3$ — and chlorine would be liberated (action similar to that of MnO_2 with hydrochloric acid). Test for the formation of chlorine by means of the odor or by using iodide starch paper. NOTE: In Experiment 1 a higher oxide of nickel was probably formed in the same manner, although to a considerably less extent.

4. Acidify solutions of potassium permanganate and potassium bichromate each with sulphuric acid, warm them and treat them with sulphur dioxide (sulphurous acid), and note any change in color. The change is due to the reduction of the given salts which are derived from the oxides Mn_2O_7 and CrO_3, respectively, to salts derived from the oxides MnO and Cr_2O_3, respectively.

Questions

In the group of elements discussed under General Questions, I, changes of valence do not occur, but the metals of the alkali and alkaline earth families show the same valence in all their compounds. Proceeding in the order in which the elements have been taken up in this book, a constantly increasing tendency is observed for the elements to display different valences, until in the group under consideration the most important chemical characteristics of the elements

are connected with their changes from one state of valency to another.
NOTE: The terms *state of valency* and *state of oxidation* can in most cases be used interchangeably.

1. In which groups of the periodic system do the elements chromium, manganese, iron, nickel, and cobalt fall? What is peculiar about the position of the last three? What other metals belong to the same family as chromium? In what relation do they stand to sulphur, selenium, and tellurium? In what relation does manganese stand to the halogens? What other elements occur in the eighth group in triads similar to iron, nickel, and cobalt?

2. How do the monoxides of chromium, manganese, iron, cobalt, and nickel compare in basic strength with the oxides of copper and zinc and with the oxides of the alkali and alkaline earth metals? How do the sesquioxides, R_2O_3, compare with the monoxides of this group as regards basic strength (see Experiment 2)?

What is true as regards the base- or acid-forming properties of the oxides higher than the sesquioxides, *e.g.*, of CrO_3, MnO_3, Mn_2O_7?

3. Give the symbols and names of salts derived from each of the three oxides of chromium, CrO, Cr_2O_3, CrO_3. In which of its compounds does chromium most resemble sulphur? iron and aluminum? nickel, cobalt, copper, and zinc?

4. Give the symbols and names of salts derived from each of the oxides of manganese, MnO, Mn_2O_3, MnO_2, MnO_3, Mn_2O_7. In which of its compounds does manganese most resemble chlorine? aluminum? cobalt, nickel, copper, and zinc? sulphur? lead in the dioxide?

5. Formulate the reaction between sulphurous acid and potassium permanganate in acid solution (see Experiment 4). By means of partial equations resolve the compounds into their constituent oxides; show the simple oxidation and

reduction, and then show how the new oxides combine to give the salts which actually result. Then add the separate equations to give the total equation for the complete reaction.

6. In the same manner formulate the reaction between sulphurous acid and potassium bichromate.

CHAPTER VII

NON-METALLIC ELEMENTS OF THE SIXTH AND SEVENTH GROUPS OF THE PERIODIC SYSTEM

The elements which are distinctly and invariably non-metallic in character are boron in the third group, carbon and silicon in the fourth group, nitrogen and phosphorus in the fifth group, oxygen, sulphur, selenium, and tellurium in the sixth group, and fluorine, chlorine, bromine, and iodine in the seventh group. It has been assumed that these elements, or at least the most important of them, were studied before entering on the course of study outlined in this book. Indeed no knowledge of the chemistry of the metallic elements would be possible without a certain knowledge of the non-metallic elements with which they form compounds.

By turning to the table of the periodic arrangement of the elements, it is at once seen that the non-metals do not occur at all in the first and second groups; that they occur only at the top in the third, fourth, and fifth groups; and that in the sixth and seventh groups they comprise all the members of the B families. It is true in these families, as might be expected by recalling characteristics of preceding groups, that the strength of the non-metallic character grows weaker and that the approach towards metallic character grows more evident, as the atomic weight increases; indeed it is probable that if the elements which should fit into the places below tellurium and iodine, respectively, are ever found, they will display quite as marked metallic properties as non-metallic.

The characteristic valences of the sixth and seventh groups are VI and VII, respectively, and the corresponding oxides are EO_3 and E_2O_7. In these oxides and in the compounds derived from them, there is little dissimilarity between the A and B families. Thus perchlorates and permanganates are in every way analogous to each other, as are also sulphates and chromates. In any lower state of valence, the elements of the B families are entirely different from those of the A families, and the most striking non-metallic properties of the former are exhibited in their ability to combine directly with metallic elements, forming oxides, sulphides, chlorides, bromides, etc. It will be noticed that the negative valence, that is, the valence exhibited towards hydrogen or a metal, is I for the non-metals of the seventh group and II for the sixth group.

Of the two most obvious possibilities for making this salt, the direct synthesis from the elements is quite impracticable, both because potassium metal is expensive and because the action would be violent and difficult to control. The method of neutralizing hydriodic acid with potassium hydroxide presents no chemical difficulties, but the materials are more costly than the iodine and potassium carbonate which are employed according to the following procedure (compare with the preparation of ammonium bromide, No. 5).

Iodine, when brought together in the presence of water with an excess of iron, reacts to form soluble ferrous iodide. By treating this solution with potassium carbonate a metathesis takes place, yielding insoluble ferrous carbonate and soluble potassium iodide. The desired product should then be obtained by filtration, except that the ferrous carbonate forms a slimy, bulky precipitate which clogs the filter; but this difficulty may be overcome if the ferrous salt is partially oxidized by adding more iodine before throwing out the iron, and the mixture of ferrous carbonate and ferric hydroxide that is obtained in this way will filter very readily.

Procedure. — Place 7 or 8 grams of iron filings and 50 cc. of water in an Erlenmeyer flask and add 25 grams of iodine, a small portion at a time, while shaking continuously. When all is added warm the mixture somewhat until all of the iodine has combined, and the dark brown color of free iodine gives place to the yellow of ferrous iodide. Filter off the excess of iron and add 5 grams more of iodine to the solution. Warm the solution until the iodine is dissolved, and then pour it into a boiling solution of 17 grams of potassium carbonate in 50 cc. of water in a good-sized

flask.   Warm the solution, which is at first very thick with
the gelatinous precipitate, until the latter becomes more
compact and the mixture thus becomes more fluid.   Filter
a little of the liquid; it should be colorless and should con-
tain no iron; otherwise a little more potassium carbonate
should be added.   Filter the whole solution and wash the
precipitate with hot water to save all the soluble salt.
Evaporate the filtrate to a small volume in a porcelain dish,
filter again if necessary, and evaporate further until crystals
begin to form.   Then leave the solution to evaporate spon-
taneously in a place protected from dust (best in a somewhat
warm place).   Collect the crystals and recover another crop
from the mother liquor.

Questions

1.   What proportion of the ferrous compound is oxidized
to ferric by the addition of the 5 grams of iodine to the
filtered solution in the foregoing procedure?

2.   On treating the mixture of ferrous iodide and iodine
with potassium carbonate, state reasons why ferrous carbon-
ate rather than ferrous hydroxide and why ferric hydroxide
rather than ferric carbonate should precipitate.

3.   Starting with iodine and potassium hydroxide, devise
a process for preparing potassium iodide without the use of
iron or similar metal.   Compare No. 5, Ammonium Bromide,
and No. 46, Potassium Bromide and Potassium Bromate.

44.   HYDRIODIC ACID

The direct synthesis of hydrogen iodide from the ele-
ments is impracticable, because the chemical affinity between
hydrogen and iodine is so small that at any temperature
sufficiently elevated to make them react at all, they would
combine only very incompletely.   By the interaction of an

iodide with a non-volatile acid, such as sulphuric acid, hydrogen iodide gas could, it is true, be formed :

$$KI + H_2SO_4 \rightarrow KHSO_4 + HI;$$
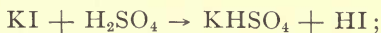
but the hydrogen iodide so formed acts as a reducing agent upon the sulphuric acid, whereby it is itself oxidized to free iodine and water.

Hydrogen iodide, then, cannot be satisfactorily prepared by the direct union of hydrogen and iodine nor by the metathesis of an iodide with the non-volatile sulphuric acid. The most convenient method of preparing it is by means of the action of hydrogen sulphide with iodine in aqueous solution :

$$H_2S + I_2 \rightarrow 2HI + S.$$
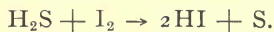
The affinity between hydrogen and sulphur is very small, as is also that between hydrogen and iodine ; but this fact, combined with the fact that free iodine is appreciably soluble while free sulphur is exceedingly insoluble in water, makes it possible for the reaction to run to completion.

The rather dilute solution of hydriodic acid which is obtained in this manner can be concentrated by distillation ; at first nearly pure water passes off, then the quantity of acid in the distillate increases until an acid of specific gravity 1.7, containing 57 per cent. of HI, comes over. At this point the distillate has the same composition as the residual liquid, and the remainder of the acid can be distilled with a constant composition. By this method it is not possible to obtain an acid of higher concentration, but by allowing this acid to absorb hydrogen iodide gas until it is saturated at 0°, an acid of specific gravity 2.0, containing 90 per cent. of HI, can be obtained. Hydrogen iodide gas can be prepared by the interaction of red phosphorus and iodine with a little water.

Procedure. — Grind 30 grams of iodine to a fine powder

and add $\frac{1}{2}$ gram of it to 100 cc. of water in a small Erlenmeyer flask. Pass hydrogen sulphide into the solution until the brown color of iodine has disappeared. Add about 1 gram more of iodine, and again pass hydrogen sulphide until the iodine is used up. After 10 grams of iodine have reacted in this way, add the remaining 20 grams and allow the mixture to stand, with repeated shaking, until the iodine is entirely dissolved (half an hour or more). Then pass hydrogen sulphide slowly until the solution is decolorized. Pour the solution into another flask, leaving the clotted lumps of sulphur behind, and rinse the first flask and the residue with a few cc. of water. Pass a current of carbon dioxide through the solution until the excess of hydrogen sulphide is entirely removed; then shake the flask vigorously to cause the suspended sulphur to clot together, and filter the solution. In this way a rather weak solution of hydriodic acid is obtained.

Fit a distilling flask with a thermometer and an inlet tube for hydrogen, and pass the side arm of the flask into a condenser. After introducing the hydriodic acid solution, fill the whole apparatus with hydrogen, and keep a slow current of this gas passing during the distillation. On distilling, nearly pure water passes over at first and the thermometer does not register appreciably above 100°. When the thermometer rises to 105° change the receiving vessel and collect the distillate until the temperature has risen to 120°. Change the receiver again and collect the rest of the distillate. The temperature rises quickly to 126°, and remains very close to this point until practically all of the acid has passed over. This last fraction is the desired concentrated acid.

Questions

1. Compare the stability of the hydrogen halides as judged (*a*) by the heat produced when they are formed

from the elements; and (*b*) by the ease with which the compounds are decomposed.

2. Compare the action of the hydrogen halides as reducing agents. Does hydrofluoric acid behave as a reducing agent towards any substance? What substances are reduced by hydrochloric acid? What substances can be reduced by hydriodic acid that are not reduced by hydrochloric acid?

3. What is the common commercial method for preparing hydrochloric acid from sodium chloride? Why could not hydrobromic or hydriodic acids be prepared in a similar manner?

4. Describe and explain the method of preparing hydrogen iodide from red phosphorus and iodine.

5. As illustrated in the foregoing preparation hydriodic acid is extremely soluble in water. A great deal of heat also is liberated when hydrogen iodide gas dissolves (19,200 calories for each mol of HI). Compare this heat effect with that of some well-known chemical reaction, for example, the neutralization of a strong acid with a strong base. In the absence of water the reaction $2HI + S \rightarrow H_2S + I_2$ takes place mainly in the direction indicated. What is the connection between the large heat effect just mentioned and the fact that the direction of the reaction is reversed when it takes place in aqueous solution?

45. POTASSIUM CHLORATE

When chlorine dissolves in water it hydrolyzes to some extent:

$$Cl_2 + HOH \rightleftharpoons HCl + HOCl \qquad (1)$$
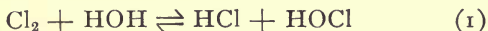
The presence of a base causes this hydrolysis to run to completion because the two acids produced by the reaction

are immediately neutralized; thus by passing chlorine into a solution of sodium hydroxide a mixture of chloride and hypochlorite is obtained:

$$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O. \quad (2)$$
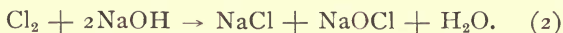
Sodium hypochlorite is fairly stable in a cold solution, but in a warm solution it is less so; it gives up its oxygen, and if no more easily oxidizable substance is present it will oxidize either chloride or hypochlorite ions to chlorate ions:

$$3NaOCl \rightarrow 2NaCl + NaClO_3 \quad (3)$$

$$or \quad 3NaOCl + KCl \rightarrow KClO_3 + 3NaCl. \quad (4)$$
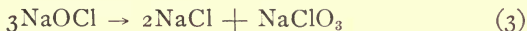
But compared with a hypochlorite (that is, the OCl^--ion), free hypochlorous acid, $HOCl$, is a far stronger oxidizing agent, and therefore the formation of chlorate takes place more readily when the solution contains a trace of acid:

$$\left. \begin{array}{l} 3HCl + 3NaOCl \rightarrow 3HOCl + 3NaCl \\ 3HOCl + KCl \rightarrow KClO_3 + 3HCl \end{array} \right\} \quad (5)$$
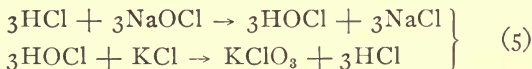
Too much acid, however, causes a reversal of reaction (1),

$$HOCl + HCl \rightarrow H_2O + Cl_2,$$
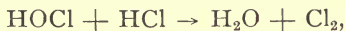
and the action either of chlorine or of hypochlorous acid on a strongly acidified solution cannot produce any chlorate.

One method for preparing potassium chlorate is to pass chlorine gas into a hot concentrated solution of potassium hydroxide until the alkali has been entirely neutralized and a small amount of free acid has been formed. This point is recognized by the solution assuming the permanent yellow tint due to free chlorine. This method is the one that will actually be used in the preparation of potassium bromate, No. 46; but in the present preparation, to avoid the use of chlorine gas, which is very objectionable in the laboratory,

bleaching powder, or calcium hypochlorite, is employed as the oxidizing agent, and potassium chloride is used in amount only sufficient to supply the necessary potassium ions.

Bleaching powder is never obtained as the pure substance represented by the chemical symbol; it always contains a considerable amount of unchanged calcium hydroxide as well as calcium carbonate. The oxidation to chlorate cannot be accomplished rapidly so long as there is any considerable amount of calcium hydroxide present, and this is therefore neutralized with hydrochloric acid. After the base is neutralized, any further addition of acid begins to react with the calcium carbonate and the escape of carbon dioxide is observed. The carbonic acid thus formed gives just about the right degree of acidity to the solution to produce the best yield of chlorate. If the hydrochloric acid is used incautiously, and more than enough to react with all the carbonate is added, a corresponding amount of chlorate will be lost, for hydrochloric acid reduces chloric acid approximately according to the reaction

$$HCl + KClO_3 \rightarrow KCl + HClO_3$$
$$HClO_3 + HCl \rightarrow H_2O + Cl + ClO_2.$$
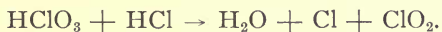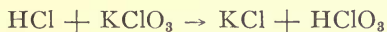
Procedure. — Wet a mixture of 175 grams of bleaching powder and 20 grams of potassium chloride, and rub it with a pestle until a smooth, thin paste is obtained. Transfer this paste to a tall bottle or jar and add hydrochloric acid (at the hood) as follows: Dilute one volume of acid of 1.12 sp. gr. with three volumes of water, and add this diluted acid very cautiously through a thistle tube, the stem of which reaches to the bottom of the liquid. Rotate the bottle or stir the contents vigorously throughout the process until carbon dioxide begins to be evolved freely. This point is recognized when with each fresh addition of $\frac{1}{2}$ to 1 cc. of acid the gas that is produced at the point where the

acid enters the liquid rises to the top without being absorbed and causes considerable frothing. Probably about 250 cc. of the 1.12 acid will be required, but this depends very largely on the quality of the bleaching powder. The reaction should now have warmed the solution to about 40°, and the formation of chlorate is nearly completed. The solution cannot be filtered at this point, as it still contains so much hypochlorous acid that it would disintegrate the filter paper. Pour it, therefore, into an evaporating dish and boil it (at the hood) until it is concentrated to a volume of about 400 cc. By this time all of the hypochlorous acid has either reacted to form chlorate or has been otherwise decomposed, and the solution may be poured through a large, common filter. Allow the filtrate to cool completely, and collect the crystals of potassium chlorate. Dissolve the crystals in hot water (see solubility table in appendix) and recrystallize twice or three times, as may be necessary to obtain the product entirely free from chloride (test with silver nitrate solution).

Questions

1. How is bleaching powder prepared? What is its formula and its chemical name?

2. Explain why the odor of chlorine becomes very noticeable when, according to the foregoing procedure, the requisite amount of hydrochloric acid has been added. Explain why addition of any further amount of acid would cause an appreciable loss of chlorine and a corresponding diminution of product.

3. How many mols of bleaching powder (assuming it to be the pure compound whose formula is given in Question 1) would be necessary to convert 1 mol of potassium chloride into chlorate? Calculate the weight of this substance that would react with the 20 grams of potassium

chloride taken, and compare this amount with the amount of bleaching powder actually taken. How much hydrochloric acid would it be necessary to use if the bleaching powder were actually this pure substance?

4. The modern commercial method of making potassium chlorate is by the electrolysis of a potassium chloride solution. What are the primary products formed at the two electrodes? Explain how the secondary reactions are similar to those outlined in the introductory discussion.

46. POTASSIUM BROMATE AND POTASSIUM BROMIDE

The reaction of bromine on solutions of caustic alkalies is almost identical to that of chlorine, and in this connection the discussion of the preparation Potassium Chlorate, No. 45, should be read. The reaction of bromine on ammonium hydroxide should also be referred to under the discussion of Ammonium Bromide, No. 5.

Bromine itself is used in this preparation, as it is not so difficult or disagreeable to handle as chlorine. By its action on concentrated potassium hydroxide solution a great deal of heat is produced, and in this hot solution any hypobromite at first formed is rapidly converted into bromate, so that as a final result 1 molecule of potassium bromate to 5 molecules of potassium bromide is obtained. By taking advantage of the great difference in the solubility of these salts, the former may be crystallized pure from the solution while the mother liquor contains all of the latter, in addition to the small amount of bromate that is soluble. The potassium bromide could not well be crystallized pure from this solution, but it is possible to reduce the bromate present to bromide by heating with charcoal and then to crystallize pure potassium bromide.

Procedure. — Dissolve 31 grams of potassium hydroxide in 31 grams of water in a 250 cc. Erlenmeyer flask. Place 40 grams of bromine (12½ cc.) in a small separatory funnel, and clamp the latter firmly in a vertical position. Place the flask in a pan of cold water, and lower the stem of the separatory funnel into the flask until it nearly reaches the surface of the solution. The funnel should now be fastened rigidly, and the flask should be floating on the surface of the bath, so that it may be held by the hand and constantly rotated. Open the stopcock of the funnel cautiously, and allow the bromine to run into the solution at the rate of 2 or 3 small drops per second. The solution should grow hot, but if the reaction becomes violent and red vapors escape from the flask, stop the flow of bromine for a few moments. The reaction is complete when the solution has acquired a permanent reddish yellow tint, due to a small excess of bromine. Cool the solution completely, collect the crystals of potassium bromate on a filter, and recrystallize them once or twice from a small amount of hot water until free from bromide (test with silver nitrate). Combine all of the mother liquors, evaporate until a pasty mass is obtained, mix this thoroughly with 5 grams of powdered charcoal, and dry the mass completely. Pulverize the dry mixture in a mortar, and then heat it to redness for an hour in a large porcelain crucible surrounded with a funnel of asbestos. Extract the product with 60 cc. of hot water, filter, wash the residue and the filter with an additional 15 cc. of hot water, and evaporate the solution to obtain crystals of potassium bromide.

Questions

1.   Write the reaction between bromine and sodium hydroxide in a cold dilute solution; in a hot concentrated solution.

2.   Why is it impossible to obtain a mixture of 5 mole-

cules of ammonium bromide and 1 molecule of ammonium bromate by the action of bromine on a warm solution of ammonium hydroxide?

3. *Test the Purity of the Potassium Bromide.* — Dissolve some of the salt in water, and acidify the solution with sulphuric acid. Appearance of the red color of free bromine indicates that the bromate was not all decomposed by the heating with charcoal. Explain and give reactions.

4. State reasons why it would not be feasible to purify the by-product, potassium bromide, by recrystallization without first decomposing the bromate.

47. POTASSIUM IODATE

As is well known, the chemical affinity of the halogens for hydrogen or positive elements decreases in passing from fluorine to iodine; but the affinity for oxygen *increases* in this order, so that iodates and iodic acid (I_2O_5) are much more stable than chlorates and chloric acid (Cl_2O_5). Use is made of this fact in the following preparation, in which the total change is represented fairly closely by the equation,

$$KClO_3 + I \rightarrow KIO_3 + Cl.$$

The actual reaction, however, is not so simple as this. The presence of a small amount of acid is necessary to make it take place. This acid gives rise to a little free chloric acid, which is a far stronger oxidizing agent than potassium chlorate, and oxidizes the iodine to iodic acid (I_2O_5). By this reaction more acid (HIO_3 or HCl) is generated, and thus the reaction when once started proceeds to completion. It will be noticed that in carrying out the following directions more iodine is taken than is necessary to react with the potassium chlorate according to the equation given above. This excess of iodine is oxidized to iodic acid by a part of

the free chlorine which is represented in the equation as escaping.

Procedure. — Dissolve 30 grams of potassium chlorate by warming it with 100 cc. of water in an 800 cc. flask. Add 35 grams of powdered iodine and hang a small funnel in the neck of the flask to prevent, to some extent, the escape of iodine vapor. Place a pan of cold water close at hand; then add 1 cc. of nitric acid (1.2) to the flask, and warm rather carefully until a brisk reaction commences. Then allow the reaction to proceed so that violet vapors fill the flask, but no appreciable quantity of iodine escapes through the funnel. If the reaction grows more violent than this, check it by dipping the flask for a moment in the cold water. When the reaction is complete, boil the solution until the last trace of iodine has disappeared. Then add 1 gram more of iodine, and boil, first in the flask and then in a beaker, until the odor of chlorine can no longer be detected. The solution now contains a considerable quantity of iodic acid in addition to the potassium iodate. Add a solution of potassium hydroxide until the neutral point is just reached (test by dipping a stirring rod in the solution and touching it to litmus paper). Allow the solution to cool, collect the crystals of potassium iodate, and evaporate the mother liquor to obtain another crop of crystals. Purify the entire product by recrystallizing once from hot water.

Questions

1. *Experiment.* — To 3 drops of potassium iodide solution in 10 cc. of water add freshly prepared chlorine water, drop by drop, until the iodine color which at first appears has been bleached. What change takes place in the state of oxidation of the iodine, first when it is liberated from the potassium iodide, and second when it is further oxidized to iodic acid? Write the equation for the latter action.

2. Dissolve a few small crystals (0.05 gram) of potassium iodate in 3 cc. of warm water, and add sulphurous acid, drop by drop, to this solution, noting the successive changes that occur until the solution again becomes clear and colorless. Trace the changes in the state of oxidation of the iodine, giving reactions, and compare with the changes in Experiment 1.

48. IODIC ACID; IODINE PENTOXIDE

Iodine pentoxide is a white solid substance that at ordinary temperatures is entirely stable. It cannot be prepared by direct synthesis from iodine and oxygen, because when cold the elements combine too slowly, and when heated the compound is decomposed into the elements. It may be readily prepared by the direct oxidation of iodine by means of strong oxidizing agents, such as concentrated nitric acid or chlorine. One method for the oxidation of iodine has already been illustrated under the preparation of Potassium Iodate, No. 47, but there the conditions were such that a salt of iodic acid was obtained rather than the free acid or its anhydride. Starting with this salt, however, the free acid is easily obtained by metathetical reactions which depend on the insolubility of barium iodate and the still greater insolubility of barium sulphate.

Procedure. — Dissolve 43 grams of potassium iodate and 26 grams of barium nitrate, separately, each in 250 cc. of hot water, and mix the two solutions at the boiling temperature while stirring well. Cool the mixture, let the heavy precipitate settle, decant off the clear liquid, and wash the salt twice by decantation with pure water. Drain the barium iodate on a Witt filter, and wash it on the filter with cold water. Then remove it to a porcelain dish, suspend it in 250 cc. of water, heat to boiling, and stir in a

solution of 15 grams of concentrated sulphuric acid (8 cc.) in 100 cc. of water. Keep this mixture well stirred at the boiling temperature for at least 10 minutes, since the conversion of solid barium iodate into solid barium sulphate is a reaction that requires some time. Filter the solution and rinse the last of the iodic acid from the solid barium sulphate by washing two or three times on the filter with small portions of water. Evaporate the solution in a casserole to a small volume, and finally, holding the casserole in the hand, keep the contents rotating, so that the whole inside of the dish is continually wet, and evaporate until solid iodic acid separates in some quantity. Cool completely and rinse the crystals with three successive portions of 10 cc. each of concentrated nitric acid (sp. gr. 1.42), triturating the crystals thoroughly with each portion of the acid. Warm the casserole carefully until the product is perfectly dry and ceases to give off acid vapors. This warming will convert the iodic acid to a large extent into the anhydride I_2O_5. Place the iodine pentoxide at once in a sample bottle or tube.

To obtain surely anhydrous iodine pentoxide, the product could be heated for some time in an oven at about 200°. Crystallized iodic acid could be obtained by dissolving the product in a very little water, in which it is extremely soluble, and allowing the solution to evaporate slowly.

Questions

1. *Experiment*. — Dissolve a little of the iodine pentoxide in water. Test the solution in such a manner as to show whether it contains a strong acid. NOTE: A test with litmus is not conclusive, for the preparation may still contain a trace of nitric or sulphuric acid which has not been completely removed.

2. *Experiment*. — Heat ½ gram of iodine pentoxide in

a dry test tube. Insert a glowing splinter in the tube.
Note whether the entire substance can be volatilized; also
if any of the original substance deposits in the cooler part
of the tube.

49. POTASSIUM PERCHLORATE

When potassium chlorate is heated to about 400° it may
decompose according to either of the following independent
reactions:

$$4KClO_3 = KCl + 3KClO_4, \qquad (1)$$

$$KClO_3 = KCl + 3O. \qquad (2)$$
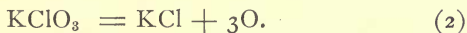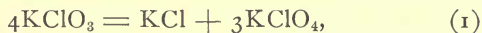
The second reaction is accelerated by catalyzers, such as
manganese dioxide or ferric oxide, or in fact any material
with a rough surface. Too high a temperature also causes
reaction (2) principally to take place. On the other hand,
if the temperature is maintained at the right point, and the
salt is free from dirt, and the inside of the crucible is per-
fectly clean and free from roughness, the decomposition
proceeds mainly according to reaction (1). Potassium per-
chlorate, being very sparingly soluble in cold water, may
easily be separated from potassium chloride and any unde-
composed potassium chlorate by means of crystallization.

Procedure. — Place 50 grams of potassium chlorate in a
dry, clean 100 cc. porcelain crucible, the glaze of which is
in perfect condition. Place a small watch glass over the
crucible to prevent loss of particles of the salt by decrep-
itation, and heat gently until the charge just melts. Then
remove the watch glass and keep the melt just hot enough
to keep up a gentle evolution of oxygen, but do not increase
the temperature when the mass shows a tendency to grow
solid. At the end of about 20 minutes the melt should
begin to solidify around the edges and should become more

or less pasty or semi-solid throughout; when this point is reached, let the contents of the crucible cool completely, then cover it with 50 cc. of water, and let it stand until it is entirely disintegrated. Collect the undissolved potassium perchlorate on a Witt filter and wash it with two successive portions of 15 cc. of cold water (see Note 5 (*a*) on page 12). Redissolve the salt in hot water (see solubility table) and allow it to recrystallize. About 30 grams of potassium perchlorate should be obtained. A few crystals of the product should give no yellow color (ClO_2) when treated with a few drops of concentrated hydrochloric acid. The product should be entirely free from chloride (test with silver nitrate).

Questions

1. Why is manganese dioxide added when oxygen is prepared by heating potassium chlorate?

2. What is the reaction of hydrochloric acid with hypochlorous, chloric, and perchloric acids, respectively?

3. What are the four oxyacids of chlorine? Compare their stability.

4. To what extent are hydrochloric, hypochlorous, chloric, and perchloric acids dissociated electrolytically in dilute solution?

5. How could pure perchloric acid be prepared from potassium perchlorate?

6. What is the solubility of silver chlorate and of silver perchlorate? How may preparations of chlorates and perchlorates be tested for the presence of chlorides?

50. SODIUM THIOSULPHATE ($Na_2S_2O_3.5H_2O$)

Sodium sulphite is a salt of the lower oxide of sulphur, and may thus be regarded as unsaturated with respect to oxygen; it is, in fact, capable of slowly absorbing oxygen

from the air and thereby going over into sulphate. If it is allowed to react with sulphur, the latter enters into the compound in much the same way as does oxygen, and *thio*sulphate instead of sulphate is formed. The sulphur so taken up certainly plays a different function from the sulphur already contained in the compound, although it is perhaps a question whether the thiosulphate is exactly the same compound as sulphate, except that one oxygen atom is replaced by a sulphur.

Sodium sulphite is conveniently prepared by allowing sulphur dioxide (sulphurous acid) to react with sodium carbonate. It is practically impossible, however, to distinguish the exact point at which the normal sulphite (Na_2SO_3) is formed; therefore it is more expedient to divide a given amount of sodium carbonate into two equal parts, to fully saturate one part with sulphur dioxide, whereby sodium bisulphite, $NaHSO_3$, is formed, and to add the other half of the sodium carbonate, thereby obtaining the normal sulphite, Na_2SO_3.

Procedure. — Dissolve 100 grams of sodium carbonate (anhydrous) in 300 cc. of hot water, and divide the solution into two equal parts. Reserve one part and place about five-sixths of the other half in one flask and the remainder in another flask. Connect these flasks in series so that sulphur dioxide gas may be passed first into the larger volume of solution, and what is there unabsorbed may pass on through the second flask. Draw the gas from a steel cylinder of liquefied sulphur dioxide, if one is available, otherwise generate it by the action of copper with concentrated sulphuric acid, and pass a vigorous stream of the gas into the solutions. After a short time a marked frothing occurs in the first flask, due to the escape of carbon dioxide, and after this frothing ceases a similar frothing soon commences in the second flask. When the latter ceases, pass

the gas a little while longer until sulphur dioxide escapes freely from the second bottle. Then place the solution of sodium bisulphite in a 600 cc. beaker, and stir in rather slowly the remaining sodium carbonate. Add 45 grams of flowers of sulphur, cover the beaker with a watch glass, and keep the mixture just barely boiling for an hour or longer. Filter the solution, concentrate it to a volume of about 200 cc., and leave it uncovered over night to crystallize in a place free from dust. Collect the crystals and obtain further crystals from the mother liquor.

Questions

1. *Experiment.* — Dissolve $\frac{1}{2}$ gram of the product in 5 cc. of water and add 2 cc. of hydrochloric acid. Observe the odor and the precipitate. What is the free acid corresponding to the salt, sodium thiosulphate? What can be said regarding the stability of this acid?

2. What is the valence of sulphur in each of the salts, sodium sulphide, sodium sulphite, and sodium sulphate? State in each case whether the sulphur plays the part of a positive or negative element.

3. Distinguish between the parts played by the two atoms of sulphur in sodium thiosulphate.

4. Give equations to represent the successive reactions that take place when sulphur dioxide is passed into a sodium carbonate solution. What stage of the process is indicated by each of the succeeding phenomena? (*a*) The gas passes into the solution in distinct bubbles and is in large part absorbed. (*b*) Effervescence takes place with minute bubbles arising from every part of the solution. (*c*) Effervescence ceases, and the gas enters the solution again in clear, distinct bubbles, but still it is for the most part absorbed. (*d*) The gas passes through the solution in distinct bubbles and is entirely unabsorbed.

GENERAL QUESTIONS. VII

NON–METALLIC ELEMENTS OF THE SIXTH AND SEVENTH GROUPS OF THE PERIODIC SYSTEM

1. What is the valence of oxygen and sulphur towards hydrogen and metallic elements? What is the valence of the halogens?

2. Give the symbols of the oxides of sulphur and of the halogens which can actually be made. State which of them are salt-forming oxides. Give the symbols of the most important oxyacids of sulphur, chlorine, bromine, and iodine, and state in each case what oxide (actual or hypothetical) is to be regarded as its anhydride.

3. Give data regarding the ease with which the hydrogen compounds of oxygen, sulphur, and the halogens can be formed; also state how readily these compounds are decomposed by heat. Draw conclusions as to the relative chemical activity of these elements when they act as negative elements.

4. Compare these hydrogen compounds with regard to their acid strength when they are dissolved in water.

5. Compare the same elements with regard to the ease with which they form compounds with oxygen, and the ease with which these compounds can be decomposed. Draw conclusions as regards the chemical activity of these elements when they act as positive elements.

6. Compare the degree of electrolytic dissociation in aqueous solution of the acids derived from the oxides, SO_2, SO_3, Cl_2O, Cl_2O_5, Cl_2O_7. When an element forms more than one oxide, which, as a general rule, has the more pronounced acid character?

APPENDIX

ADDITIONAL GENERAL QUESTIONS

I. ALKALI AND ALKALINE EARTH METALS

1. What are the symbols of the oxides of sodium and potassium in which these metals undoubtedly display their ordinary valence of one? How can these oxides be prepared, using the peroxides as a starting point? How can they be prepared from the hydroxides or from the nitrates?

2. What oxide is obtained by burning sodium in the air? What relation does this oxide bear to hydrogen peroxide? What is supposed to be the molecular structure of a peroxide?

3. What is the difference in meaning between the terms *base* and *alkali*?

4. Distinguish between a *mild* alkali and a *caustic* alkali.

5. Explain why solutions of the carbonates of sodium and potassium behave as mild alkalies.

6. Judged by its composition, sodium bicarbonate is an acid salt. Explain why in spite of this fact its solution behaves as a mild alkali.

7. What is the difference between ammonia and ammonium? How can ammonia be set free from ammonium salts?

8. In its compounds the ammonium radical, NH_4, behaves similarly to the metals of the alkali group. It is not unreasonable to suppose that if ammonium could be isolated, it would show properties similar to those of sodium

and potassium when in the metallic state. To what extent is this supposition borne out by the facts?

9. Why is the alkaline strength of an ammonium hydroxide solution greatly reduced by the addition of an ammonium salt?

10. Give an outline of the modern method for preparing the alkali metals and the alkaline earth metals. What are the most characteristic properties of these metals?

11. What are the chief differences between the properties of the alkali and alkaline earth metals (compare potassium with calcium)?

12. Tabulate the solubilities of the hydroxides, carbonates, and sulphates of the alkaline earth metals, and observe in what sense the solubility changes with increasing atomic weight of the metal in each series of salts.

II. ELEMENTS OF THE THIRD GROUP OF THE PERIODIC SYSTEM

1. Give the formulæ of normal boric and aluminic acids; of the meta acids; of the anhydrides; and of the sodium salts of tetraboric acid, aluminic acid, and met-aluminic acid.

2. All of the alums are isomorphous. What is isomorphism? Give the name and symbol of at least two alums which contain neither aluminum nor potassium.

It is not possible to prepare an alum from boron in which this element plays the part of aluminum in common alum. What is the fundamental difference between boron and aluminum which accounts for this difference in behavior?

3. Before the use of the electrolytic process, what metal was used to reduce the oxide of aluminum in the preparation of metallic aluminum?

4. Describe the principle of the alumino-thermic processes.

5. Why would it not be possible to prepare metallic calcium by means of the alumino-thermic process?

6. What other metals could be substituted for aluminum in the alumino-thermic process?

7. *Experiment.* — To a solution of any aluminum salt (use common alum), add a solution of sodium carbonate.

What is the gas evolved, and what is the precipitate? Why is it impossible for aluminum carbonate to form under these conditions?

III. HEAVY METALS OF THE FIRST TWO GROUPS OF THE PERIODIC SYSTEM

1. Cite facts which show the difference in chemical activity between the elements of Family A and of Family B in Group I.

2. Compare the chlorides of copper, silver, and gold (copper and gold each possess two chlorides) with regard to their solubility and the valence of the metal. Which of the chlorides are characteristic of the position of these elements in Group I?

3. Starting with an alloy of copper and silver, devise a method for obtaining the two metals separately in the metallic condition.

4. *Experiment.* — Prepare cuprous oxide by reducing a cupric salt with grape sugar in an alkaline solution. To 20 cc. of a 10 per cent. solution of copper sulphate add 50 cc. of water, and then stir in 20 cc. of a 10 per cent. solution of sodium hydroxide; add a solution of grape sugar until a deep blue color appears and the precipitate of cupric hydroxide has nearly or quite dissolved; lastly, warm the mixture gently until a yellow and then a clear, bright red precipitate is obtained. Collect this precipitate of cuprous oxide on a filter and wash it with water. Treat the cuprous

oxide on the filter with dilute sulphuric acid, and examine
the solution formed and the insoluble residue to determine
what products are formed in the reaction. Explain how
one-half of the cuprous oxide is oxidized at the expense of
the other half which is reduced.

5. *Experiment.* — Add a little cupric salt solution to
a potassium iodide solution, and test a drop of the resulting
liquid for the presence of free iodine. What is the precipi-
tate? Rinse it free from the dark-colored solution in order
to observe its own color. Write the reaction, and explain
how the copper salt has acted as an oxidizing agent.

6. Compare the chlorides of zinc, cadmium, and mer-
cury (mercury has two chlorides) as regards their solubility
and the valence of the metal.

7. In which of their compounds do zinc, cadmium,
and mercury most resemble each other, and thus justify
their classification in the same family of the periodic system?

8. In what important respects do these metals differ
from the alkaline earth metals which form the other family
in the second group of the elements?

9. Given an alloy of zinc cadmium and mercury, how
might one proceed ·to obtain the three separately in the
metallic condition?

10. *Experiment.* — Prepare a dilute acidified solution of
zinc sulphate, using 10 cc. of a 10 per cent. solution and
adding 20 cc. of water and 5 cc. of sulphuric acid (1 : 4).
Divide the solution into two parts, and treat one part with
hydrogen sulphide and the other part with ammonium
sulphide.

Explain why the solubility product of zinc sulphide is
exceeded in the one case and not in the other.

11. *Experiment.* — Saturate with hydrogen sulphide an
unacidified solution of zinc sulphate (made by diluting 5 cc.
of the 10 per cent. solution with 10 cc. of water), when

saturated the solution will continue to smell of hydrogen sulphide after closing the mouth of the tube with the thumb and shaking. Filter off the precipitate, and test for zinc ions in the filtrate by adding ammonium sulphide.

Explain the cause of the incompleteness of this reaction.

12. *Experiment.* — Modify the last experiment by dissolving 3 grams of solid sodium acetate in the solution before saturating with hydrogen sulphide. Do any zinc ions pass into the filtrate in this case? How is the difference in the results explained?

13. *Experiment.* — Dilute 5 cc. of a 10 per cent. solution of cadmium chloride or cadmium sulphate with 10 cc. of water, and saturate with hydrogen sulphide. Filter off the precipitate, and test for cadmium ions in the filtrate by adding ammonium sulphide.

Saturate with hydrogen sulphide a similar solution of cadmium salt after first adding 10 cc. of hydrochloric acid (1.12 sp. gr.).

How do the solubility products of cadmium and zinc sulphides compare with each other?

14. Find out from the text-book, or by experiment, whether the sulphides of mercury, copper, and silver can be precipitated from moderately acidified solutions. Compare these sulphides with those of zinc and cadmium with respect to their solubility products.

15. Solutions of mercuric chloride and mercuric cyanide are poor conductors of electricity. To what general rule do these salts thus form an exception?

IV. ELEMENTS OF THE FOURTH GROUP OF THE PERIODIC SYSTEM

1. Why is carbon of importance in the organic world? With what other elements is carbon found in combination in organic compounds?

2. In what compounds does carbon most frequently occur in rocks?

3. What is the relation between an ortho and a meta acid? Give symbols of ortho and meta silicic, stannic, and plumbic acids.

4. *Experiment.* — Add hydrochloric acid to a solution of sodium silicate (water glass). What is the gelatinous substance obtained, and what change would it undergo if dried and baked?

5. Name some of the common minerals that consist of some form of silicic acid or its anhydride.

6. With what bases is silicic acid most commonly found in combination in the minerals that constitute our common rocks?

7. Place tin and lead approximately in their places in the electromotive series of the metals. Explain why either of these metals will react slowly with hydrochloric acid but rapidly with nitric acid.

8. By what oxidizing agents can a stannous compound be converted into a stannic? By what means can a stannic compound be reduced to a stannous?

9. Under what conditions can lead in the plumbous state be oxidized to the plumbic state? Is this as easily accomplished as the corresponding oxidation of stannous to stannic tin? Under what conditions does lead dioxide act as an oxidizing agent? (See Experiment 4 under Lead Dioxide, page 95.)

10. Show how the action of the common lead storage battery depends upon changes in the state of oxidation of lead.

11. Show how the mixed oxides of lead, Pb_2O_3 and Pb_3O_4, may be regarded as salts of ortho and meta plumbic acid.

12. Find out the following facts either from a text-book

or by means of experiment: What is the color and what is the chemical formula of the precipitates formed when hydrogen sulphide is passed into solutions of $PbCl_2$, $SnCl_2$, and $SnCl_4$, respectively? Are all of the lead and tin thrown out in this way from faintly acidified solutions? Does precipitation occur in solutions strongly acidified with hydrochloric acid?

Compare lead sulphide and stannous sulphide with the sulphides of other heavy metals in regard to their solubility product.

13. If a precipitate was obtained containing sulphides of both tin and lead, how might it be treated in order to separate the two metals? (See Experiment 2 under Stannic Sulphide, page 89.)

V. ELEMENTS OF THE FIFTH GROUP OF THE PERIODIC SYSTEM

1. Describe the physical properties of the pure trichlorides of phosphorus, arsenic, and antimony. Compare the properties of these compounds with those of the tetrachlorides of carbon, silicon, and tin. Are such chlorides of the metalloids to be regarded as salts?

2. What is the behavior of the trichlorides of phosphorus, arsenic, antimony, and bismuth when treated with water? Show how their varying behavior corresponds with the increasing metallic properties of the elements.

3. Give reasons why arsenic and antimony should be classed as metals; as non-metals. Which one of the metals studied under Group IV also falls into the transitional class between metals and non-metals?

4. Distinguish between ortho, meta, and pyro phosphoric acids. To which of these acids does nitric acid correspond in structure?

Which of the antimonic acids yields a sparingly soluble sodium salt?

5. Distinguish between phosphorous and phosphoric acids.

Give equations to show reactions in which nitrous, phosphorous, and arsenious acids act as reducing agents. Give an example of the action of arsenic acid as an oxidizing agent.

6. What is meant by antimonyl and bismuthyl salts? Give symbols and describe their properties. By what other names are bismuthyl nitrate and antimonyl chloride known?

7. Arsenic pentasulphide can be slowly precipitated by leading hydrogen sulphide into a solution of arsenic acid containing a large amount of concentrated hydrochloric acid. Does this fact give any indication of the extent to which the ion As^{+++++} is capable of existing in solution?

VI. Heavy Metals of the Sixth, Seventh, and Eighth Groups of the Periodic System

1. What is the valence of the metal in the oxides Mn_3O_4 and Fe_3O_4? Explain in what sense these oxides may be regarded as salts.

2. *Experiment. — Oxidation of Manganous Salts to Permanganate in Acid Solution:* To half a test tube of water add 3 drops of a manganous sulphate solution and 10 cc. of nitric acid. Then add $\frac{1}{2}$ gram of lead dioxide and boil the mixture. Let the solid settle, and observe the color of the clear solution.

Explain why the presence of hydrochloric acid would prevent the formation of the red color. Recall the action of hydrochloric acid with potassium permanganate.

3. *Experiment. — Oxidation of a Chromic Salt in Alkaline Solution:* To a little of a chromic salt solution add

three times its volume of 10 per cent. sodium hydroxide solution. Warm the mixture and pass in chlorine until the color has become a clear yellow. Compare this action with the action of hydrochloric acid with sodium chromate, and explain how the different conditions make these practically opposite reactions possible.

4. Write the reactions for the oxidation of a ferrous salt by (*a*) nitric acid; (*b*) bromine; (*c*) potassium permanganate. Write the reactions for the reduction of a ferric salt by (*d*) hydrogen sulphide; (*e*) sulphur dioxide; (*f*) stannous chloride.

5. From what oxide of iron are the ferrates derived, and is this oxide acidic or basic in character? Can the oxide itself be prepared? How is potassium ferrate prepared? With what compounds of chromium and manganese is it analogous in composition?

6. Show that chromium exists in the same state of oxidation in both chromates and bichromates. In what respect do these salts differ from each other?

Show that on the other hand manganates and permanganates are derived from different oxides of manganese.

7. What salt is formed by treating 1 mol of potassium sulphate with 1 mol of sulphuric acid? How does this salt resemble and how differ from the salt obtained by treating 1 mol of potassium chromate with 1 mol of chromic acid?

VII. Non–Metallic Elements of the Sixth and Seventh Groups of the Periodic System

1. The tension of the elements chlorine, bromine, iodine, and sulphur, to pass into the form of simple negative ions in aqueous solution, decreases in the order given. Describe simple experiments which show the correctness of this statement.

2. *Experiment.* — *Reduction of any Oxysalt of Sulphur.*
Mix a little sodium sulphate (or any oxysalt of sulphur) with
twice its amount of sodium carbonate; moisten the mixture,
so that some of it may be made to adhere to the charred end
of a burnt match. Heat the mixture on the match end in
the reducing part of a Bunsen flame until the salt melts.
Detach the end of the match with the fused salt, and place
it on a bright silver coin, together with 1 drop of water.
After a few moments observe the dark fleck on the coin.
Explain the reactions involved in the test.

3. Would it be feasible to reduce sodium sulphate with
charcoal as an industrial method of preparing sodium sul-
phide? Discuss the relative advantages of this and other
possible methods.

4. If it were desired to reduce potassium chlorate to
chloride, why would it be unsafe to mix it with charcoal
and heat? Why does not the same danger exist with sodium
sulphate?

5. *Experiment.* — Agitate a few grains (0.05 gram) of
iodine with 2 cc. of water. To what extent does the iodine
dissolve? Add a few crystals of potassium iodide (0.1 gram),
and observe whether any more of the iodine passes into solu-
tion. Account for the increased solubility of the iodine.
What are polyiodides?

6. *Experiment.* — Treat $\frac{1}{2}$ gram of powdered sulphur
with 5 cc. of a colorless solution of sodium or ammonium
sulphide. What is a polysulphide? To a solution of a
colorless sulphide add hydrochloric acid until the solution
is acid to litmus. Treat in the same way some of the
polysulphide just prepared and compare the results.

7. When a solution of potassium iodide is exposed to
the action of the oxygen of the air no change takes place.
When, on the other hand, a solution of hydriodic acid is
exposed to the same conditions, iodine is slowly displaced

and the solution becomes brown, due to the liberated iodine. Show by writing the ionic reactions that when iodine is displaced by oxygen, either hydrogen ions must be used up or hydroxyl ions must be produced, and that therefore the reaction is favored by the presence of the former and retarded by the presence of the latter.

8. Write reactions in which sulphuric acid acts as an oxidizing agent; in which sulphurous acid acts as a reducing agent; in which sulphurous acid acts as an oxidizing agent; in which hydrogen sulphide acts as a reducing agent.

9. Write reactions in which hydriodic, hydrobromic, and hydrochloric acids act as reducing agents; in which the oxyacids of the halogens (take, for example, hypochlorous, chloric, and iodic acids) act as oxidizing agents. Explain in what way these reactions are of the same character as these written under Question 8.

INTERNATIONAL ATOMIC WEIGHTS, 1915

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.0
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Nitrogen	N	14.01
Beryllium	Be	9.1	Osmium	Os	190.9
Bismuth	Bi	208.0	Oxygen	O	16.00
Boron	B	11.0	Palladium	Pd	106.7
Bromine	Br	79.92	Phosphorus	P	31.0
Cadmium	Cd	112.40	Platinum	Pt	195.0
Cæsium	Cs	132.81	Potassium	K	39.10
Calcium	Ca	40.09	Praseodymium	Pr	140.6
Carbon	C	12.00	Radium	Ra	226.4
Cerium	Ce	140.25	Rhodium	Rh	102.9
Chlorine	Cl	35.46	Rubidium	Rb	85.45
Chromium	Cr	52.0	Ruthenium	Ru	101.7
Cobalt	Co	58.97	Samarium	Sa	150.4
Columbium	Cb	93.5	Scandium	Sc	44.1
Copper	Cu	63.57	Selenium	Se	79.2
Dysprosium	Dy	162.5	Silicon	Si	28.3
Erbium	Er	167.4	Silver	Ag	107.88
Europium	Eu	152.0	Sodium	Na	23.00
Fluorine	F	19.0	Strontium	Sr	87.62
Gadolinium	Gd	157.3	Sulphur	S	32.07
Gallium	Ga	69.9	Tantalum	Ta	181.0
Germanium	Ge	72.5	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.0	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.42
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.85	Tungsten	W	184.0
Krypton	Kr	83.0	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.2
Lead	Pb	207.10	Xenon	Xe	130.7
Lithium	Li	7.00	Ytterbium (Neoytterbium)	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.0			

PERIODIC ARRANGEMENT OF THE ELEMENTS

Group / Highest Oxide	O (E)	I-A (E_2O)	I-B	II-A (EO)	II-B	III-A (E_2O_3)	III-B	IV-A (EO_2)	IV-B	V-A (E_2O_5)	V-B	VI-A (EO_3)	VI-B	VII-A (E_2O_7)	VII-B	VIII (EO_4)
First Short Period	He (4)		Li (7)		Be (9.1)		B (11)		C (12)		N (14)		O (16)		F (19)	
Second Short Period	Ne (20)		Na (23)		Mg (24.3)		Al (27.1)		Si (28.3)		P (31)		S (32.1)		Cl (35.5)	
First Long Period	A (39.9)	K (39.1)	Cu (63.6)	Ca (40.1)	Zn (65.4)	Sc (44.1)	Ga (69.9)	Ti (48.1)	Ge (72.5)	V (51.2)	As (75)	Cr (52)	Se (79.2)	Mn (54.9)	Br (79.9)	Fe (55.9) Co (59.0) Ni (58.7)
Second Long Period	Kr (83)	Rb (85.5)	Ag (107.9)	Sr (87.6)	Cd (112.4)	Yt (89)	In (114.8)	Zr (90.6)	Sn (119)	Cb (93.5)	Sb (120.2)	Mo (96)	Te (127.5)	—	I (126.9)	Ru (101.7) Rh (102.9) Pd (106.7)
Third Long Period	Xe (130.7)	Cs (132.8)	Au (197.2)	Ba (137.4)	Hg (200)	La (139)	Tl (204)	Ce[*] (140.3)	Pb (207.1)	Ta (181)	Bi (208)	W (184)	—	—	—	Os (190.9) Ir (193.1) Pt (195)
				Ra (226.4)				Th (232.4)				U (238.5)				

* Between Cerium and Tantalum lie a number of elements which are very similar to each other in properties and which, together with Yttrium, Lanthanum, and Cerium, which they much resemble, constitute the so-called rare earth elements.

TABLE OF SOLUBILITIES[1]

In the following tables are given data which should be useful in connection with the preparations and questions in this book.

The formulæ given are those of the crystallized compounds which most readily separate from aqueous solution at the laboratory temperature, but it should be remembered that many salts have several hydrates, and it has often been difficult to decide which one to place in the table.

In the second column the behavior of the crystallized salt when it is exposed to the air of the laboratory is indicated: **s = unchanged by exposure to atmosphere; e = efflorescent; d = deliquescent; d, e = deliquescent or efflorescent, according as to whether the humidity is above or below the average; CO_2 = absorbs carbon dioxide and falls to a white powder; Ox = compound is oxidized, especially in presence of moisture.**

In the third column are given the figures for the solubility at $0°$, $25°$, and $100°$, except in the cases in which other temperatures are indicated in parenthesis. Fractions have, as a rule, been dropped in giving the solubilities.

[1] Much of the data in this table has been obtained from Seidell, Solubilities of Inorganic and Organic Substances.

Salt.	Formula of crystallized salt.	Behavior when exposed to atmosphere.	Solubility in Water.	
			Grams anhydrous salt per 100 grams water in a saturated solution at 0° 25° 100°	Mols per liter of solution at laboratory temperature.
Aluminum:				
chloride,	$AlCl_3.6H_2O$	.. d ..	.... (15°) 70	 4
nitrate,	$Al(NO_3)_3.9H_2O$	.. d ..	very soluble	
sulphate,	$Al_2(SO_4)_3.18H_2O$	.. s ..	..31 ......38..... 89 ..	.... 0.8
Ammonium:				
acetate,	$NH_4C_2H_3O_2$	.. d ..	very soluble	
bromide,	NH_4Br	.. s ..	(10°) 66 (30°) 81 (100°) 128	 6
chloride,	NH_4Cl	.. s ..	..29 ......39..... 77 ..	5
nitrate,	NH_4NO_3	.. d ..	. 118..... 214 ....871..	11
Antimony:				
chloride,	$SbCl_3$	.. d ..	} hydrolyzes with water to insoluble basic salt; very soluble in acids	
sulphate,	$Sb_2(SO_4)_3$	.. d ..		
sulphide,	Sb_2S_3	.. s ..	insoluble; soluble in concentrated acids	
Arsenic:				
sulphide,	As_2S_3	.. s ..	insoluble in water or acids; soluble in alkalies	
Barium:				
carbonate,	$BaCO_3$.............	.. s ..	.... 0.0023	.. 0.00011
chloride,	$BaCl_2.2H_2O$	.. s ..	..32 ......37..... 59 ..	.... 1.7
chromate,	$BaCrO_4$	.. s ..	.... 0.0004	.. 0.000015
hydroxide,	$Ba(OH)_2.8H_2O$	CO_2	(0°) 1.7 (25°) 4.7 (80°) 101	.... 0.2
iodate,	$Ba(IO_3)_2.H_2O$	.. s ..	.0.008....0.03.....0.2..	.....0.001
nitrate,	$Ba(NO_3)_2$	.s, d ..	..5......10.....34 ..	.... 0.3
sulphate,	$BaSO_4$	.. s ..	.......0.00023........	.. 0.000010
sulphite,	$BaSO_3$	.. s ..	..(20°) 0.020 (80°) 0.002..	....0.001
sulphide,	$BaS.6H_2O$	. Ox .	very soluble; hydrolyzes to $Ba(SH)_2$ and $Ba(OH)_2$	
Bismuth:				
chloride,	$BiCl_3$	.. d ..	} hydrolyzes with water to insoluble basic salt; very soluble in acids	
nitrate,	$Bi(NO_3)_3.5H_2O$	.. d ..		
sulphate,	$Bi_2(SO_4)_3$	.. d ..		
sulphide,	Bi_2S_3	.. s ..	insoluble in acids or alkalies	
Cadmium:				
chloride,	$CdCl_2.2\frac{1}{2}H_2O$	.. e ..	(0°) 90.(18°) 110. (100°)147	 5
nitrate,	$Cd(NO_3)_2.4H_2O$	.. d ..	(0°) 110.(18°) 127..(60°) 326	.... 4.3
sulphate,	$CdSO_4.2\frac{2}{3}H_2O$	.. e ..	(0°) 76..(40°) 79.. (100°) 61	 2

Salt. Formula of crystallized salt.	Behavior when exposed to atmosphere.	Solubility in Water. Grams anhydrous salt per 100 grams water in a saturated solution at 0° 25° 100°	Mols per liter of solution at laboratory temperature.
Cadmium:			
sulphide, CdS	.. s ..	insoluble; soluble in concentrated acids	
Calcium:			
carbonate, $CaCO_3$.............	.. s ..	.... 0.0013	...0.00013
chloride, $CaCl_2.6H_2O$	.. d ..	..60......88 .....159..	.....5.2
chlorate, $Ca(ClO_3)_2.2H_2O$	.. d ..	...... (18°) 178	.....5.3
chromate, $CaCrO_4.2H_2O$......	.. e ..	..11......12 ......3...	.....0.8
fluoride, CaF_2	.. s ..	.... 0.0016	... 0.0002
hydroxide, $Ca(OH)_2$..........	CO_2	. 0.19.... 0.16 ....0.08 .	.... 0.02
nitrate, $Ca(NO_3)_2.4H_2O$	.. d ..	...... (18°) 122	.....5.2
oxalate, $CaC_2O_4.H_2O$	.. s ..	.... 0.0007	.. 0.00004
sulphate, $CaSO_4.2H_2O$	.. s ..	.0.18 .... 0.21 ... 0.16..	... 0.015
sulphite, $CaSO_3$	......	........0.004........	...0.0003
Chromium:			
chloride, $CrCl_3.6H_2O$	.. d ..	..........130	8
nitrate, $Cr(NO_3)_3.9H_2O$	......	very soluble; melts 36.5°	
sulphate, $Cr_2(SO_4)_3.18H_2O$.....	. s, e .	..........120	4
Cobalt:			
carbonate, $CoCO_3$	.. s ..	insoluble; soluble in acids	
chloride, $CoCl_2.6H_2O$	.. s ..	..42......53 .....104..	3
nitrate, $Co(NO_3)_2.6H_2O$	.. d ..	....(0°)84 (91°)340	.... 4.3
sulphate, $CoSO_4.7H_2O$	.. s ..	..26......39 ..... 83 ..	2
sulphide, CoS	.. s ..	insoluble in water or dilute acids	
Copper:			
carbonate, $CuCO_3$.............	.. s ..	insoluble; soluble in acids	
chloride, $CuCl_2.2H_2O$	. s, d .	..71......79 .....108..	.... 5.0
nitrate, $Cu(NO_3)_2.6H_2O$	e melts 38°	..82..... 150.....275..	.... 4.8
sulphate, $CuSO_4.5H_2O$	. s, e .	..14......23 ..... 75 ..	.... 1.2
sulphide, CuS	.. s ..	insoluble in water or acids	
Hydrogen:			
arsenic acid, $H_3AsO_4.\frac{1}{2}H_2O$ ...	.. d ..	very soluble; melts 35.5°	
boric acid, H_3BO_3.............	.. s ..	. 2.0......4.7.... 27.5..	.... 0.6
iodic acid, HIO_3	. d, s .	..........300	
oxalic acid, $H_2C_2O_4.2H_2O$	.. s ..	(0°) 3.5 (25°) 11.4 .. (70°) 64	.... 0.9

Salt.	Formula of crystallized salt.	Behavior when exposed to atmosphere.	Solubility in Water. Grams anhydrous salt per 100 grams water in a saturated solution at 0° 25° 100°			Mols per liter of solution at laboratory temperature.

Hydrogen:
  phosphoric acid, H_3PO_4 ...... | .. d .. | very soluble; melts 37°

Iron:
  chloride (ous), $FeCl_2.4H_2O$ .... | .. d .. | ..(15°) 67 .... (80°) 100..
  (ic), $FeCl_3.6H_2O$ ..... | .. d .. | very soluble; melts 31°
  carbonate (ous), $FeCO_3$ ...... | .. s .. | insoluble; soluble in acids
  nitrate (ous), $Fe(NO_3)_2.6H_2O$.. | Ox | .... (18°) 82 ....
  (ic), $Fe(NO_3)_3.9H_2O$ ... | .. d .. | very soluble; melts 47°
  sulphate (ous), $FeSO_4.7H_2O$ .. | e, Ox | (0°) 16 .. (30°) 33 ... (90°) 43 | 2
  (ic), $Fe_2(SO_4)_3$ ...... | .. d .. | very soluble
  sulphide .... | .. s .. | insoluble; soluble in acids

Lead:
  acetate, $Pb(C_2H_3O_2)_2.3H_2O$ .. | .. s .. | .... 50..... 200.. | 1.5
  bromide, $PbBr_2$ .... | .. s .. | .. 0.5..... 1.0..... 4.8 .. | 0.02
  carbonate, $PbCO_3$ .... | .. s .. | ...... 0.0001 .... | .. 0.000003
  chloride, $PbCl_2$ .... | .. s .. | .. 0.7..... 1.1..... 3.3 .. | 0.05
  hydroxide, $Pb(OH)_2$ .... | | .... 0.01 .... | .. 0.0004
  iodide, PbI_2 .... | .. s .. | .. 0.04 ... 0.08 .... 0.44 .. | ... 0.002
  nitrate, $Pb(NO_3)_2$ .... | .. s .. | ... 38..... 59..... 132.. | 1.4
  sulphate, $PbSO_4$ .... | .. s .. | .... 0.004 .... | .. 0.00013
  sulphide, PbS .... | .. s .. | insoluble; soluble in concentrated strong acids

Lithium:
  carbonate, Li_2CO_3 .... | .. s .. | .. 1.5..... 1.3..... 0.7 .. | 0.17
  bicarbonate, $LiHCO_3$ .... | .. s .. | ...... (13°) 5.5 .... | 0.8
  chloride, $LiCl$ .... | .. d .. | .. 67..... 82..... 128.. | .. 13.3
  hydroxide, $LiOH.H_2O$ .... | CO_2 | .. 12.7 ... 12.9 .... 17.5 .. | 5.0
  nitrate, $LiNO_3.3H_2O$ .... | .. d .. | (0°) 54 (30°) 138 (70°) 176 | 7.3
  sulphate, Li_2SO_4 .... | .. s .. | ... 35..... 34..... 30 .. | 2.8

Magnesium:
  carbonate, $MgCO_3.3H_2O$ ..... | .. s .. | .... 0.2......... | 0.01
  chloride, $MgCl_2.6H_2O$ .... | .. d .. | ... 53..... 57..... 73 .. | 5.1
  hydroxide, $Mg(OH)_2$ .... | CO_2 | .... 0.001 .... | .. 0.0002
  nitrate, $Mg(NO_3)_2.6H_2O$ ...... | .. d .. | .. (0°) 67 ...... (40°) 85 .. | 4.0
  sulphate, $MgSO_4.7H_2O$ ...... | .. e .. | ... 27..... 39..... 74 .. | 2.8

Manganese:
  carbonate, $MnCO_3$ .... | .. s .. | insoluble; soluble in acids
  chloride, $MnCl_2.4H_2O$ .... | . e, d .. | ... 63..... 77..... 115.. | 5

Salt. Formula of crystallized salt.	Behavior when exposed to atmosphere.	Solubility in Water.		
		Grams anhydrous salt per 100 grams water in a saturated solution at 0° 25° 100°		Mols per liter of solution at laboratory temperature.
Manganese:				
nitrate, $Mn(NO_3)_2.6H_2O$	.. d ..	(0°) 102 (25°) 166 (35.5) 331		 5
sulphate, $MnSO_4.5H_2O$	. s, e .	.. 53..... 65 ..... 32 ..		 4
sulphide, MnS...............	. Ox .	insoluble; soluble in dilute acids		
Mercury:				
chloride (ous), $HgCl$...........	.. s ..	.... 0.0002		.. 0.00001
(ic) $HgCl_2$	.. s ..	..3.7 .....7.4..... 61 ..		.... 0.2
iodide (ic), HgI_2	.. s ..	........0.005.........		...0.0001
nitrate (ous), $HgNO_3.H_2O$	. s, e .	very soluble in a little water much water ppts. basic salt very soluble in HNO_3		
(ic), $Hg(NO_3)_2.\frac{1}{2}H_2O$...	.. d ..			
sulphate (ous), Hg_2SO_4	.. s ..	........0.006.........		...0.0001
sulphide (ic), HgS.............	.. s ..	insoluble; insoluble in concentrated acids		
Nickel:				
carbonate, $NiCO_3$	.. s ..	insoluble; soluble in acids		
chloride, $NiCl_2.6H_2O$	. s, d .	.. 54..... 67 ..... 88 ..		 4
nitrate, $NiNO_3.6H_2O$	. s, d .	(0°) 80 .(20°) 96 (95°) 233		 6
sulphate, $NiSO_4.7H_2O$	.. e ..	(0°) 27..(30°) 43...(99°) 77		 2
sulphide, NiS...............	.. s ..	insoluble in water or dilute acids		
Potassium:				
acetate, $KC_2H_3O_2$	.. d ..	(5°) 188 (14°) 230 (62°) 492		25
bromate, $KBrO_3$	.. s ..	..3.1 .....8.0..... 50 ..		....0.38
bromide, KBr	.. s ..	.. 54 .....68 .....104..		..... 4.6
carbonate, $K_2CO_3.1\frac{1}{2}H_2O$.....	.. d ..	.. 89 .... 113.....156..		..... 5.9
(bi) carbonate, $KHCO_3$........	.. s ..	(0°) 22..(25°) 36...(60°) 60		.... 2.8
chlorate, $KClO_3$	.. s ..	..3.1 .....8.2..... 56 ..		....0.52
chloride, KCl	.. s ..	.. 28 .....36 ..... 57 ..		.... 3.9
chromate, K_2CrO_4	.. s ..	.. 59 .....64 ..... 79 ..		.... 2.7
(bi) chromate, $K_2Cr_2O_7$	.. s ..	...5......16 ..... 89 ..		.... 0.4
fluoride, $KF.2H_2O$	.. d ..	.......(18°) 92		....12.4
hydroxide, $KOH.2H_2O$	.. d ..	.. 97 .... 119.....178..		18
iodate, KIO_3	.. s ..	..4.7 .....9.9..... 32 ..		....0.35
iodide, KI	.. s ..	..128..... 148.....208..		..... 6.0
manganate, K_2MnO_4	.. d ..	very soluble		
nitrate, KNO_3.................	.. s ..	.. 13 .....37 .....246..		..... 2.6
oxalate, $K_2C_2O_4.H_2O$	.. s ..	.........38...........		.... 1.6
perchlorate, $KClO_4$............	.. s ..	.........1.5...........		....0.11
permanganate, $KMnO_4$	.. s ..	(0°) 2.8..(25°) 8.0 ..(65°) 25		....0.33

Salt.	Formula of crystallized salt.	Behavior when exposed to atmosphere.	Solubility in Water.	
			Grams anhydrous salt per 100 grams water in a saturated solution at $0°$ $25°$ $100°$	Mols per liter of solution at laboratory temperature.
Potassium:				
sulphate, K_2SO_4		s ..	...7......12 ..... 24 ..	.... 0.62
(bi) sulphate, $KHSO_4$			$(0°)$ 36..$(20°)$ 51 .$(100°)$ 122	.... 3.5
sulphide, $K_2S.5H_2O$..........		d ..	very soluble	
sulphite, $K_2SO_3.2H_2O$........		d ..	very soluble	
Silver:				
acetate, $AgC_2H_3O_2$		s ..	$(0°)$ 0.7. $(25°)$ 1.1.. $(80°)$ 2.5	.... 0.06
bromide, $AgBr$		s ..	........0.00001........	. 0.0000006
carbonate, Ag_2CO_3 ....:....		s ..	........0.003........	...0.0001
chlorate, $AgClO_3$		s ..	........15	.... 0.6
chloride, $AgCl$		s ..	.... 0.0002	.. 0.00001
chromate, Ag_2CrO_4		s ..	........0.002........	.. 0 00015
fluoride, AgF................		d ..	...... $(16°)$ 182	....13.5
iodate, $AgIO_3$		s ..	........0.005........	.. 0.00014
iodide, AgI		s ..	.......0.0000003.......	.0.00000001
nitrate, $AgNO_3$		s ..	..122.... 257.....952..	.... 8.4
oxide, Ag_2O, dissolves as $AgOH$		s ..	.... 0.0025	...0.0002
perchlorate, $AgClO_4$..........		d ..	very soluble	
sulphate, Ag_2SO_4		s ..	..$(18°)$ 0.73 ...$(100°)$ 1.5 ..	... 0.024
sulphide, AgS...............		s ..	insoluble in water or acids	
Sodium:				
acetate, $NaC_2H_3O_2.3H_2O$......		s, e ..	$(0°)$ 34..$(25°)$ 53...$(40°)$ 65	 6
(tetra) borate				
(borax), $Na_2B_4O_7.10H_2O$....		s ..	$(5°)$ 1.3 .$(30°)$ 3.9 ..$(100°)$ 53	...0.15
bromide, $NaBr.2H_2O$		s ..	.. 73 .....87 .....118..	.... 6.9
carbonate, $Na_2CO_3.10H_2O$		e ..	..7.0 .....28 ..... 46 ..	.... 1.8
(bi) carbonate, $NaHCO_3$		s ..	$(0°)$ 6.9..$(25°)$ 10..$(60°)$ 16	.... 1.1
chlorate, $NaClO_3$		s ..	.. 82.....105.....233..	.... 6.4
chloride, $NaCl$		s ..	.. 36 .....36 ..... 40 ..	.... 5.4
chromate, $Na_2CrO_4.10H_2O$.....		e ..	$(0°)$ 32..$(21°)$ 90 $(100°)$ 126	.... 3.3
(bi) chromate, $Na_2Cr_2O_7.2H_2O$		d ..	..$(0°)$ 163.... $(98°)$ 433 ..	.. 5 0
fluoride, NaF		s ..	........$(21°)$ 4.2	.... 1.1
hydroxide, $NaOH.H_2O$		d ..	.. 42.....114.....348..	 21
iodide, $NaI.2H_2O$		e, d ..	.159.....184.....302..	.... 8.1
nitrate, $NaNO_3$		s ..	.. 73 .....92 .....178..	.... 7.4
oxalate, $Na_2C_2O_4$		s ..	..$(15°)$ 3.2 ....$(100°)$ 6.3 ..	...0.24
permanganate, $NaMnO_4.3H_2O$		d ..	very soluble	
sulphate, $Na_2SO_4.10H_2O$		e ..	$(0°)$ 5.0$(32.75°)$ 50.65$(100°)$ 43	.... 1.2
(bi) sulphate, $NaHSO_4.H_2O$ ...		d ..	..$(25°)$ 29..... $(100°)$ 50 ..	

Salt.	Formula of crystallized salt.	Behavior when exposed to atmosphere.	Solubility in Water.			Mols per liter of solution at laboratory temperature.
			Grams anhydrous salt per 100 grams water in a saturated solution at			
			0°	25°	100°	
Sodium:						
sulphide, $Na_2S.9H_2O$		{ Ox } d, e		very soluble		
sulphite, $Na_2SO_3.10H_2O$		.. e ..	(0°)14..(20°)27...(40°)50			 2
thiosulphate, $Na_2S_2O_3.5H_2O$ ..		s, e	(10°)60..(25°)76..(45°)124			 5
Strontium:						
carbonate, $SrCO_3$		.. s ..	.........0.001.........			.. 0.00007
chloride, $SrCl_2.6H_2O$		.. e ..	.. 44 .....56 .....101..			.... 3.0
hydroxide, $Sr(OH)_2.8H_2O$		CO_2	..0.4 .....1.0.....32 ..			....0 06
nitrate, $Sr(NO_3)_2.4H_2O$		.. e ..	.. 40 .....79 .....101..			.... 2.7
sulphate, $SrSO_4$.....,.........		.. s ..	.... 0.01			...0.0006
Tin:						
chloride (ous), $SnCl_2.2H_2O$....		{ s } Ox	.. (0°)84..... (15°)270 ..			 7
Zinc:						
carbonate, $ZnCO_3$.............		.. s ..	.... 0.004 ?			.. 0.0003 ?
chloride, $ZnCl_2.3H_2O$..........		.. d ..	..208.... 432.....615..			.... 9.2
nitrate, $Zn(NO_3)_2.6H_2O$		.. d ..	.. 95 .... 127..........			.... 4.7
sulphate, $ZnSO_4.7H_2O$		.. e ..	.. 42 . . .58..... 81 ..			.... 3.1
sulphide, ZnS		.. s ..	insoluble; soluble in acids			

SUPPLEMENT

In the preparation of the third edition of Synthetic Inorganic Chemistry it has seemed desirable to proceed slowly in order not to be confronted too soon after the completion of the edition with the desirability of making further alterations and additions.

This supplement to the Second Edition is therefore printed that the Author may have the opportunity to test new ideas in his own classes and that other users of the book may have the benefit of new work which has already seemed to justify itself.

DIRECTIONS FOR WORK

Preliminary Report. — Before beginning work on a preparation the student should have a clear knowledge of the whole procedure and should understand the reactions involved as well as the application of chemical principles to these reactions.

To that end study carefully the general discussion of the preparation as well as the procedure. Then write in the notebook all reactions, and, starting with the given amount of the principal raw material, calculate what amounts of the other substances are necessary to satisfy the equations. When the amount specified in the directions is different from that calculated, state the reason for the difference. Calculate also on the basis of the equations the amount of the main product as well as of any important intermediate products or by-products.

Present this preliminary report to an instructor and obtain his approval before beginning operations.

Manipulation. — All references from the procedure to the general notes on laboratory manipulation should have been studied before making the preliminary report. Indeed the instructor will probably make sure by a quiz that this has been done before he accepts the preliminary report.

Laboratory Record. — The working directions, in the section entitled *procedure*, are to be kept at hand while carrying out the manipulations. These directions do not need to be copied in the laboratory notebook; but it is essential, nevertheless, to keep a laboratory record in which are entered all important observations and data; such as, for example,

appearance of solutions (color, turbidity); appearance of precipitates or crystals (color, size of grains, crystalline form); results of all weighings or measurements; number of recrystallizations; results of tests for purity of materials and products, etc.

Questions. — The section under this title gives suggestions for study, which involves: (1) laboratory experiments and direct entries in the laboratory notebook; (2) consultation of reference books, of which all that are necessary will be found upon the shelf in the laboratory; (3) original reasoning.

The answers to the questions should be written in the laboratory notebook following the entries for the exercise, and this book should be submitted at the same time as the preparation for the approval of an instructor.

General Questions. — Besides the specific study questions for each preparation there are, accompanying each group of exercises, general questions relating to the whole group; and these are to be worked out by every student. The answers to these questions are to be written on a certain prescribed kind of paper and handed in at the office, neatly bound, within the times which will be posted.

Use of Time in Laboratory. — In preparation work it is frequently necessary to wait for considerable periods of time for evaporations, crystallizations, etc., to take place. This time may be utilized for work upon the study questions and experiments, but even then it is advisable to have usually more than a single preparation under way. Thus no time need be wasted by the energetic student who plans his work well.

Yield of Product. — Where possible the methods employed in these preparations resemble those actually used on an industrial scale; where this is, however, impossible on the limited scale of the laboratory, mention is made of the fact, with reasons therefor. On account of the limitations con-

nected with work on a laboratory scale, it is of course impossible to get as high percentage yields as could be obtained on a large commercial scale. The amounts obtained of each preparation are to be weighed and recorded, but the chief stress is to be laid upon the excellence of the product rather than upon its quantity.

NOTES ON LABORATORY MANIPU–
LATION

12. AUTOMATIC GAS GENERATOR

FOR HYDROGEN, HYDROGEN SULPHIDE, OR CARBON DIOXIDE.

Supplies: 1 300-cc. generator bottle (thick walled).
1 calcium chloride drying tube (10 inches long exclusive of stem; 1 inch internal diameter).
1 reservoir of 300 cc. capacity.
1 2-hole rubber stopper to fit generator bottle.
1 1-hole rubber stopper to fit drying tube.
1 foot rubber tube to connect generator bottle and reservoir.
glass wool.

This apparatus is based on the principle of the familiar Kipp generator and it is especially suited to cases in which a solution is to be saturated with the gas in question, as, for example, when an ammoniacal solution of common salt is to be saturated with carbon dioxide in the preparation of sodium bicarbonate by the Solvay process.

Directions for Setting up and Starting the Generator. — Assemble the apparatus as shown in the diagram. The stem of the generator tube E should reach flush with the bottom of the stopper but not below. The delivery tube C should reach nearly to the bottom of the generator bottle D. Place the requisite amount of calcium carbonate (or zinc, or ferrous sulphide) in the generator tube. Then insert a loose plug of glass wool F about $1\frac{1}{2}$ inches long so that it will stand about

midway between the top of the solid material and the stopper in the mouth of the tube, and act as a gas filter (to remove acid spray). Pour the requisite amount of acid into the
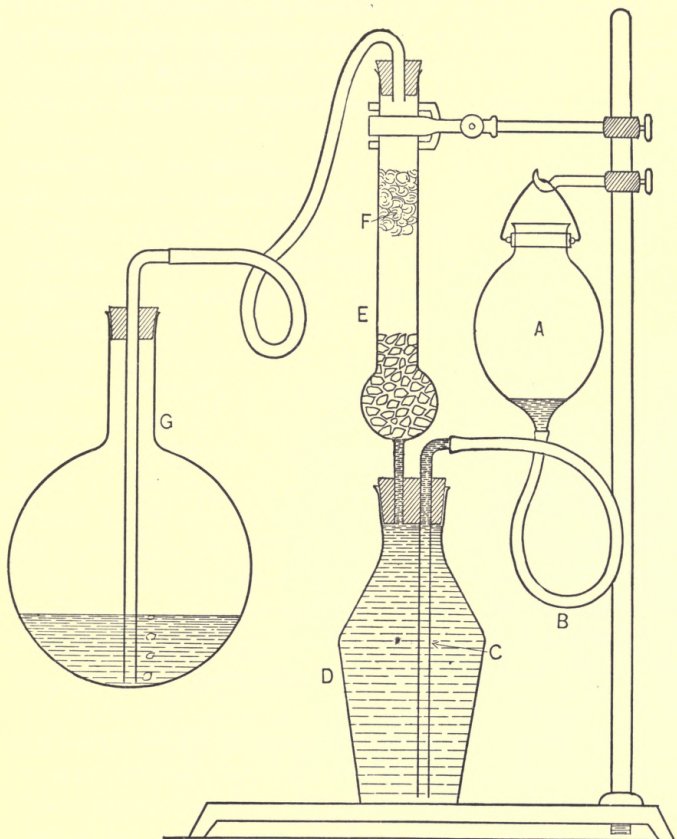
AUTOMATIC GENERATOR

reservoir A; clamp the reservoir at just the same height as the generator tube and pour in water cautiously until the acid rises and barely touches the solid in the generator tube.

The generation of gas will now begin and proceed automatically. Do not pour any more water into the reservoir until the air is swept from the receiving flask and the mouth of the latter is closed tight (see below). Then add not more than 5 cc. of water. Later after the vigor of the absorption has slackened the reservoir may be raised to a higher level to give a greater pressure and some more water may be added.

If the solid charge or the acid becomes exhausted, lower the reservoir to a little below the generator tube; remove the stopper from the generator tube and introduce more of the solid if necessary; if the acid needs renewal, unclamp the reservoir, lower it and invert it to let the spent liquor siphon out of the generator bottle, and refill with acid as in the first charging.

Directions for Using the Generator. — Place the solution to be saturated in a flask (*G* in diagram) fitted with a 1-hole rubber stopper through which passes a delivery tube reaching to the bottom of the flask. Start the generator in action (see directions above). Loosen the stopper in the flask a little so that gas escapes until all the air originally in the generator and receiving flask is swept out. Then make the stopper tight; the gas will now pass in as rapidly as it can be absorbed by the solution. Shaking the receiving flask will greatly increase the rapidity of absorption, but observe this *caution:*
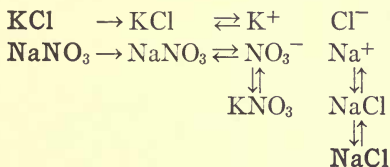
At the outset if the gas is drawn too rapidly the liquid may rise so far in the generating tube E as to produce too violent an action, which will either blow out the stoppers, or cause froth to pass over into the receiver. Therefore be cautious not to sweep out the air too rapidly, and after the stopper is placed firmly in the receiving flask be cautious during the first 15 minutes not to shake the receiver too strongly.

1. POTASSIUM NITRATE FROM SODIUM NITRATE AND POTASSIUM CHLORIDE

Read the discussion on pages 25–26 of the second edition.

In the following procedure equi-molal amounts of sodium nitrate and potassium chloride are taken and enough water added to dissolve at the boiling temperature all of the sodium nitrate taken or all of the potassium nitrate which could result from metathesis, but not enough to dissolve either the potassium chloride taken nor the sodium chloride which could be formed by metathesis. Nevertheless after this mixture is boiled a short time all of the solid potassium chloride disappears and the only solid salt left is sodium chloride.

The mechanism of the chemical process may be more easily appreciated if it is represented on paper in the following fashion:

$$\mathbf{KCl} \quad \rightarrow KCl \quad \rightleftarrows K^+ \quad Cl^-$$
$$\mathbf{NaNO_3} \rightarrow NaNO_3 \rightleftarrows NO_3^- \quad Na^+$$
$$\Updownarrow \qquad \Updownarrow$$
$$KNO_3 \qquad NaCl$$
$$\Updownarrow$$
$$\mathbf{NaCl}$$

The formulas printed in bold face type stand for the substances in the solid state, — those in common type for substances in the dissolved state. Single arrows indicate that the reaction runs to completion in that direction under the conditions prevailing (the boiling temperature is supposed to be prevailing in the above representation). The double arrows indicate that an equilibrium is reached and no substance shown on either side of the arrows disappears from the sphere of action. If the conditions were to be shown at 0° solid potassium nitrate would have to be indicated in equilibrium with the dissolved salt.

Materials: crude Chili saltpeter $NaNO_3$, 100 grams.
crude potassium chloride KCl, 88 grams.

Reagent: 1% $AgNO_3$ solution.

Apparatus: 350-cc. casserole.
watch glass.
5-inch funnel.
perforated filter plate.
800-cc. suction bottle and pump.
platinum wire.

Procedure. — Place 100 grams $NaNO_3$ and 88 grams KCl in a 350-cc. casserole. Add 125 cc. of water, cover with a watch glass, and place over a low flame. Keeping an eye on the casserole to see that the contents do not boil, prepare a suction filter according to Note 4 (b), on page 7. Then raise the flame under the casserole and watch it until boiling commences. Lower the flame and let the mixture boil gently just one minute, keeping the watch glass over the casserole to prevent too much evaporation of water. While it is at the boiling temperature, pour (see Figure 1, page 6) the mixture from the casserole onto the suction filter after first starting a gentle suction. Quickly scrape most of the damp salt onto the filter and suck out as much of the liquid as possible. Then return the solid salt, which is mostly NaCl, to the casserole. Pour the solution into a beaker and cool it to 15° or below by setting it in a pan of cold water or snow. Separate the crystals of KNO_3 from the cold liquor by means of the suction filter, observing last sentence of Note 3 on page 7, and pour the liquor into the casserole containing the first crop of NaCl crystals. Bring the solution to boiling point and boil gently three minutes without a watch glass over the casserole, thus allowing some of the water to escape by evaporation. Then filter at the boiling temperature exactly as in the first instance. Cool the filtrate and collect a second crop of KNO_3 crystals, adding them to the first crop and

pouring the liquor into a flask labelled " Mother Liquors."
Examine the two kinds of crystals, tasting them and using
a microscope. Draw pictures in the notebook of the crys-
tals as seen in the microscope. Dissolve about o.1 gram
of the supposed KNO_3 in 2 cc. of water and test for chloride
by adding 1 drop of $AgNO_3$ solution. Considerable chloride
will be found and the product must be purified by recrys-
tallization. Weigh the crystals roughly while they are still
moist, add one half their weight of hot water, and warm until
solution is complete. Cool to below $15°$ and separate the
crystals from the mother liquor, adding the latter to the
reserve flask. Test as above to see if this crop of crystals
is free from chloride. If not repeat the recrystallization as
many times as is necessary to get a perfectly pure product.
A little of this when dissolved should give no turbidity with
silver nitrate solution, and when held in the flame on a plati-
num wire should color it the violet color characteristic of
potassium with none of the yellow sodium color. Spread the
preparation on filter paper or an unglazed porcelain plate
and allow it to dry by standing exposed to the air; then put
up the salt in a test tube or a small bottle and label it neatly.
If the final yield of pure product is not satisfactory in amount
the collected mother liquors should be boiled down to about
100 cc., and used as the starting point in a repetition of the
above procedure. 30 grams may be regarded as a very
satisfactory yield.

The sequence of the operations in this preparation can be
followed rather more readily in the tabulated procedure
shown on the following page.

TABULATED PROCEDURE

Treat 100 grams $NaNO_3$ and 88 grams KCl with 125 cc. water; heat to boiling and boil one minute; filter hot.   Do not rinse out dish but keep it for second boiling.

On filter: NaCl, dirt, some KNO_3: transfer back to dish in which first boiling was made (1)	Filtrate: cool and filter			
	Crystals: impure KNO_3 (2)	Filtrate is saturated with KNO_3 and NaCl. Pour into dish in which original mixture was boiled and to which impure NaCl (1) was added. Bring to boil, boil 3 minutes, and filter hot.		
		On filter: NaCl and dirt fairly free from KNO_3 (3)	Filtrate: cool and filter	
			Crystals: impure KNO_3 (4)	Filtrate is saturated with KNO_3 and NaCl. Save temporarily in flask labelled "Mother Liquors" (5)

RECRYSTALLIZATION

Unite impure KNO_3 (2) and (4); heat with one half their weight of water until dissolved; cool and filter.

Crystals: Nearly pure KNO_3. Recrystallize repeatedly until entirely pure, adding all mother liquors to (5) in the reserve flask.	Filtrate contains nearly all of the NaCl from the impure product, and is saturated with KNO_3; add to (5) in the reserve flask.

Discard mother liquors (5) if the yield of pure KNO_3 is satisfactory.

Questions

1. Define metathesis.

2. When a metathetical reaction is carried out in the *wet way*, why is the solubility of the substances involved of importance? Explain why, according to this point of view, the reactions $AgNO_3 + KCl = AgCl + KNO_3$ and $BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$ are much more complete than the reaction $NaNO_3 + KCl = KNO_3 + NaCl$.

3. Explain why fewer operations should be required to prepare potassium nitrate from potassium sulphate and barium nitrate than by the foregoing procedure.

4. Explain why all of the solid salt should change to NaCl when the original materials are boiled with insufficient water to dissolve all of either the NaCl or the KCl.

5. In the tabulated procedure what is the advantage of adding the impure NaCl (1) to the second mother liquor instead of discarding it?

3. SODIUM BICARBONATE BY THE AMMONIA (SOLVAY) PROCESS.

Read the discussion on pages 31, 32 of the Second Edition.

Materials: table salt, 59 grams.

14-normal ammonium hydroxide, 71 cc.

cracked marble, 105 grams.

12-normal hydrochloric acid, 175 cc.

Apparatus: automatic gas generator (see Note 12 on p. 192 of Supplement).

suction filter (see Note 4, a and b on p. 7).

750-cc. flask equipped with 1-hole rubber stopper, delivery tube reaching to bottom, and 18 inches of rubber delivery tube.

300-cc. flask with stopper.

Procedure. — Place the salt, the ammonium hydroxide, and 130 cc. of water in the smaller flask and shake vigorously until the salt is dissolved. Pour the solution through a filter into the 750-cc. flask (large plaited filter for speed). Use this flask as the absorption vessel and connect it with the carbon dioxide generator. Charge the generator with the cracked marble and hydrochloric acid and proceed to saturate the solution with carbon dioxide following with care the directions for starting and using the generator (Note 12). After 10 minutes commence shaking the flask

very cautiously and after 5 minutes more, if it is found to be safe, shake vigorously. Let the absorption continue until practically no more gas passes into the absorption flask even with vigorous shaking. If the shaking has been continuous, this point will be reached within one hour. It is equally as well to allow the absorption to proceed by itself over night and to shake next day to complete the saturation with the gas. When the absorption is complete collect the precipitated sodium bicarbonate on the suction filter (Notes 3, 4a, and 4b), drain it thoroughly with suction, stop the suction, pour over the surface of the product 15 cc. of cold water, and after this has soaked in apply the suction again. Wash a second time with 15 cc. of cold water exactly as at first. Spread the drained product on a clean unglazed porcelain plate (or on filter paper spread on a folded newspaper) and leave it 24 hours to dry. Test the preparation for chloride by dissolving about 0.1 gram in a little water, acidulating slightly with nitric acid, and adding a drop of silver nitrate solution. There will be considerable clouding.

Questions

1. What is the purpose of washing the product with water? How much sodium bicarbonate is lost in this way (see solubility table)?

2. Why must the solution be acidulated with nitric acid before testing with silver nitrate?

3. Why does shaking greatly increase the rate of absorption?

4. How do you explain the heat produced in the absorption flask?

5. How can you prepare sodium carbonate from sodium bicarbonate?

6. Why cannot potassium bicarbonate be effectively prepared from potassium chloride by the ammonia process?

(Look up the solubility of potassium bicarbonate.) What process may be used to prepare potassium carbonate from this source?

7. What is an acid salt? How does a solution of an acid salt such as $KHSO_4$ behave toward litmus? Test the behavior of solutions of $NaHCO_3$ and Na_2CO_3 toward litmus. Explain the cause of this behavior.

8. Would a precipitate of sodium bicarbonate form if carbon dioxide were passed into a solution of sodium chloride alone? Explain the part played by the ammonia in the formation of the product.

9. Explain how a given amount of ammonia may be used over and over again.

3–A. SODIUM CARBONATE FROM SODIUM BICARBONATE

Heat the sodium bicarbonate obtained in No. 3 until it is converted into sodium carbonate. Compare the weight obtained with that calculated.

3–B. CAUSTIC SODA FROM SODIUM CARBONATE

Apparatus: 8-inch dish.
suction filter.
burette with normal HCl.
15-cc. pipette.
500-cc. bottle with rubber stopper.

Read the discussion and procedure of No. 2, Caustic Potash from Wood Ashes, and adapt that method to the conversion into sodium hydroxide of the sodium carbonate obtained in No. 3–a. Keep the sodium hydroxide solution in the rubber stoppered bottle.

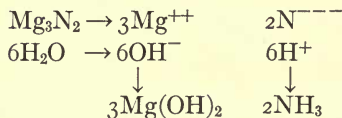Answer Questions 1 and 2 under No. 2.

5. AMMONIUM BROMIDE

The solution contains practically pure ammonium bromide all of which should be recovered. Evaporate to complete dryness and pulverize the caked salt thereby obtained. If preferred the first part of the evaporation may be hastened by heating to gentle boiling with a small flame held constantly in the hand. It is unsafe to put a flame under the dish and leave it, for the solution may "bump" and spatter. Furthermore as soon as the salt is dry it will volatilize freely itself.

5-A. MAGNESIUM NITRIDE AND AMMONIUM SALT FROM ATMOSPHERIC NITROGEN

Active metals, as those of the alkali and alkaline earth families, when heated, combine readily with nitrogen. In this preparation powdered magnesium in a closely packed mass is allowed to react with air. The oxygen reacts with the upper layers and only nitrogen penetrates to the interior of the mass. Thus a large part of the magnesium should be converted to nitride. On treatment with water the substance hydrolyzes and the ammonia given off can be absorbed in an acid to yield ammonium salt.

The mechanism of the hydrolysis of magnesium nitride is probably similar to that of such salts as sodium carbonate and ferric chloride, and it would therefore appear as follows:

$$
\begin{array}{ccc}
Mg_3N_2 \rightarrow 3Mg^{++} & & 2N^{---} \\
6H_2O \rightarrow 6OH^- & & 6H^+ \\
\downarrow & & \downarrow \\
3Mg(OH)_2 & & 2NH_3
\end{array}
$$

If magnesium nitride can ionize at all the ions which it would yield are obviously Mg^{++} and N^{---} as shown in the upper horizontal equation. The fact that such an ion as N^{---} is entirely unfamiliar does not weaken our belief in

the above mechanism, because, as the direction of the arrow shows, the N^{---} ion is formed only to be removed according to the right-hand vertical equation.

Materials: powdered magnesium, 10 grams.
          dry sand, 50 grams.
Apparatus: iron crucible and cover of 25 cc. capacity.
          300-cc. r.b. flask.
          50-cc. distilling flask.
          filter bottle (or 500-cc. flask).
          U-tube $\frac{7}{8}$ inches wide, $7\frac{1}{2}$ inches tall.
          2 thistle tubes.
          1 pinch cock.
          2 2-hole rubber stoppers.
          1 1-hole rubber stopper.
     See diagram for fittings.

Procedure. — Weigh an iron crucible of about 25 cc. volume together with the cover. Pack it even full with powdered magnesium, tapping the crucible on the desk to make the powder settle. Weigh the filled crucible; it should hold 10 grams of the powder. Place the cover tightly on top, surround the crucible with a cylinder of asbestos $2\frac{1}{2}$ to 3 inches in diameter so as to diminish the loss of heat by radiation. Heat the crucible as hot as possible with a Tirrell burner for 45 minutes. After it cools empty the crucible onto a piece of paper and note the white MgO on top and the yellow Mg_3N_2 beneath. Place the material in a mortar, break up the lumps, add 25 grams of dry coarse sand, and mix well. Then place 25 grams of sand in the bottom of a dry 300-cc. flask and pour the mixture from the mortar on top of it. Use this as the generating flask A in the diagram. Have the rest of the apparatus and connections fitted as in the diagram. Pour 50 cc. of water into the absorption flask E. The water should seal the bottom of the thistle
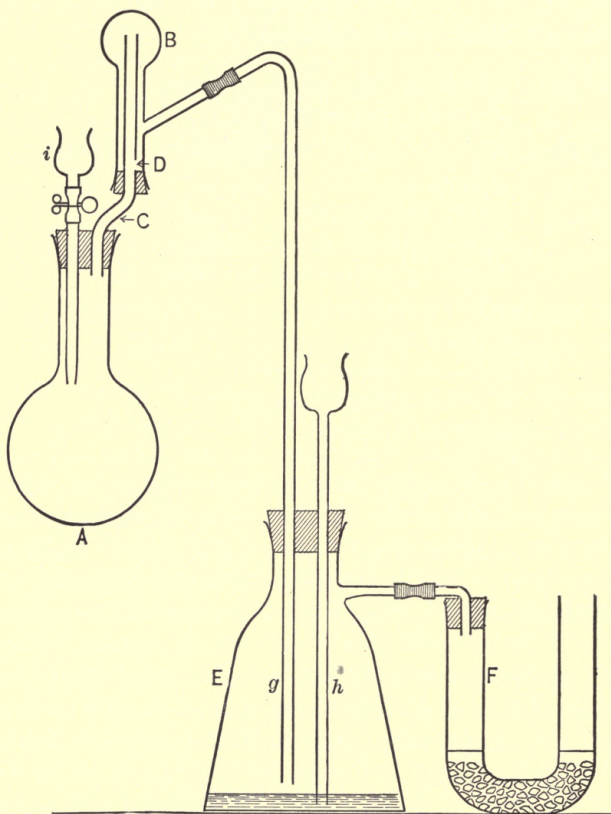
APPARATUS FOR DISTILLATION OF AMMONIA FROM MAGNESIUM NITRIDE

A = Generating flask. B = Trap to catch solid matter entrained with gas and steam. C = Connecting tube of $\frac{1}{4}$-inch internal diameter. D = Hole for return of solid and condensed water to flask. E = Absorption flask with pure water in bottom. F = Absorption tube, bend sealed with dilute acid; glass beads are an advantage.

tube h but should stand about $\frac{1}{4}$ inch below the end of the delivery tube g. Place 10 cc. of 6-normal HCl in the absorption tube F and then add enough water to seal the bend. Remove the stopper and fittings from the generating flask A. Pour water into the thistle tube i and open the pinch cock until the stem of the tube has filled with water. Replace the stopper in the flask and open the pinch cock to admit a single drop of water. Add another drop as soon as the reaction subsides and continue to add a single drop at a time until the reaction becomes less violent. Finally add enough water to make 70 cc., rock the flask until the contents are thoroughly mixed, then while still rocking the flask apply a small flame until the liquid boils. Boil gently for 15 minutes. Pour together the contents of the absorption flask and the absorption tube, and, using litmus as an indicator, add enough more 6-normal HCl to just neutralize the ammonia. Evaporate the solution to obtain solid ammonium chloride, following the directions for Ammonium Bromide on page 202 of this Supplement.

Questions

1. *Experiment.* — Burn a little calcium in the air and test the ash for nitride. How?

2. Give reasons for regarding the action of magnesium nitride with water as an example of hydrolysis. Remember that hydrolysis is the exact reverse of neutralization and produces an acid and a base from a salt and water. What is the acid and what is the base in this case?

3. Why is it necessary to mix the magnesium nitride with an inert material such as sand before adding water?

4. The layer from the top of the crucible will often contain a black substance as well as a white, and particularly so if the gases from the flame entered under the lid of the crucible. What is this black substance and why should it have formed?

5. On the basis that air contains 4 volumes of nitrogen to 1 volume of oxygen figure what fraction of the magnesium would be converted to nitride under the most favorable conditions.

6 and 8. TO DRY THE PREPARATIONS OF STRONTIUM HYDROXIDE AND BARIUM HYDROXIDE

Spread the moist crystals in a layer $\frac{1}{4}$ inch deep on a large sheet of filter paper. Press with another filter paper, then fold the edges of the lower paper up tightly over the crystals and set the whole away in the cupboard (never in a heated place) until the next exercise. The moisture is drawn through the paper by capillarity and evaporates from the outside, while the paper to a large extent prevents the carbon dioxide from reaching the preparation.

9. BORIC ACID

Procedure. — Dissolve 100 grams of borax $Na_2B_4O_7.10H_2O$ in 300 cc. of boiling water. Add a few drops of methyl orange solution (a dye which is yellow in neutral or alkaline solution but is pink in distinctly acid solution) and add 12-n HCl until the color of the dye has changed through an orange to a distinct pink and addition of 1 cc. more of the acid does not increase the pink tone. Let the solution cool to 15° or below, drain the crystals on a suction filter. If the filtrate is not distinctly pink (showing it to be acid) add enough 12-n HCl to make it so, shake vigorously, and add any crystals thus obtained to the main crop. Dissolve the crystals in 300 cc. of boiling water, filter if not clear, crystallize by slow cooling with occasional stirring if crystals cake together too much. Collect the crystals and let them dry at room temperature.

Note. — The above procedure yields fine granular crystals. Lustrous flaky crystals can be obtained if a little grease is

present in the crystallizing solution. To this end dissolve
1 gram of soap shavings in 300 cc. of boiling water and use
this solution to dissolve the boric acid for the recrystallization.
This procedure is not recommended if purity of product is
required rather than an attractive appearance.

11-A. ALUMINUM NITRIDE AND AMMONIA FROM ATMOSPHERIC NITROGEN

In a recently developed process named after the inventor,
Serpek, aluminum oxide and carbon are heated in an electric
furnace in an atmosphere of nitrogen (or rather of producer
gas, which contains nitrogen and carbon monoxide). The
reaction is essentially as follows:

$$Al_2O_3 + N_2 + 3 C \rightarrow 2 AlN + 3 CO.$$
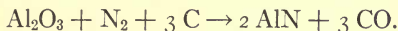
Now it is well known that aluminum oxide cannot be re-
duced to metal by means of carbon but that, at very high
temperature the oxygen may be withdrawn and carbon sub-
stituted for it, thus yielding the carbide:

$$2 Al_2O_3 + 9 C \rightarrow Al_4C_3 + 6 CO.$$
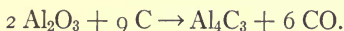
In an atmosphere of nitrogen, however, the place of that
part of the carbon that unites with the aluminum may be
taken by the nitrogen, and aluminum nitride is thus obtained.

The manipulation of a powerful enough electric furnace
on a small scale for a laboratory preparation is scarcely feasi-
ble. But if we start with metallic aluminum instead of the
oxide we may easily effect its combination with nitrogen.

Materials: finely powdered aluminum, 16 grams. The ma-
terial sold for use as pigment and often labelled
Aluminum Bronze, although it is nearly pure
aluminum, is suitable for the purpose. The oil
which still adheres from the grinding is of no
disadvantage.

Materials: lamp black $\frac{3}{4}$ gram.

sodium hydroxide, 30 grams. Use material which comes in sticks or large lumps. It should contain at least 95% of NaOH and not more than a trace of carbonate. Avoid the granulated material for this preparation.

Apparatus: iron crucible and cover of 25 cc. capacity.

dark-colored goggles (recommended to protect the eyes from the blinding light).

1000-cc. round bottom flask.

50-cc. distilling flask.

filter bottle (or 500-cc. flask).

U-tube $\frac{7}{8}$ inches wide, $7\frac{1}{2}$ inches tall.

1 thistle tube.

1 2-hole rubber stopper.

2 1-hole rubber stoppers.

See diagram under No. 5–a for assembling the apparatus. A larger generating flask A is used. The stem of the thistle tube i reaches to bottom and the stop cock is dispensed with. The safety tube h in absorption flask is unnecessary.

Procedure. — Mix the 16 grams of aluminum and $\frac{3}{4}$ gram of lamp black thoroughly by grinding together in a mortar. Place the mixture in the iron crucible, packing it down as compactly as possible by tapping the crucible on the desk top. The joint of the cover should be fairly tight to exclude air during the preliminary heating. If a little moist shredded asbestos is packed around under the edge of the cover before the latter is pressed down onto the crucible, such a tight joint is obtained. Heat the crucible with a Tirrell burner rather cautiously at first until the oil upon the aluminum has ceased to give off inflammable gas. Then set the Tirrell burner under the crucible and start heating the top of cover with a blast lamp. When the cover is bright red remove

the lamp from underneath; keep heating the cover as strongly as possible until the under part of crucible has cooled so that it is no longer visibly red. Remove the cover quickly and play the tip of blast flame upon one part of the surface of the charge until it ignites and becomes blindingly incandescent. The reaction is then self-sustaining and will spread gradually to every part of the crucible.

After examining the cooled product in the crucible pulverize it and transfer it to the generating flask. Place 75 cc. of water in the absorption flask and 30 cc. of 6-normal H_2SO_4 in the absorption tube. Add 50 cc. of water to the generating flask. Make sure that this flask is supported in such a way that a pan of cold water can be raised from underneath to cool the flask whenever the reaction becomes violent and has to be checked. Dissolve 30 g. of NaOH in 50 cc. of water and add 10 cc. of this solution to the generating flask. Warm this flask until a vigorous reaction begins. Remove the flame and add the rest of the NaOH little by little. Thereupon warm the flask during $\frac{1}{2}$ hour just enough to keep the contents boiling gently. It is now well to let the flask cool a little and to leave it stoppered over night. It may then be reconnected and boiled for 15 minutes. If this is not feasible the boiling should be continued immediately for another $\frac{1}{2}$ hour. Save the solution remaining in the flask as the starting material for the next preparation. Unite the contents of the absorption flask and absorption tube, and add enough more 6-n H_2SO_4 to just neutralize the ammonia. Be careful not to add a drop too much of the H_2SO_4 because it cannot be removed by evaporation, — it is well to hold a part of the solution in reserve in case the neutralization of the main part is slightly overstepped. Evaporate the solution to obtain solid ammonium sulphate, following the direction for Ammonium Bromide on page 202 of this Supplement,

Questions

1. Powdered aluminum, unmixed with carbon, does not enter into rapid self-sustaining action with the elements of the air. Why might one expect that such a reaction would take place? Then how may one explain its not reacting according to expectation? Finally how can you account for the fact that a small admixture of soot makes an energetic reaction possible?

2. What information did you obtain in your tests of the gas passing unabsorbed through the U-tubes? What probably is the gas and how do you account for its formation? (Look up Aluminum Carbide in reference book.)

3. Compare the hydrolysis of aluminum nitride with that of magnesium nitride in No. 5. Can you offer any plausible explanation why the hydrolysis of the latter takes place so much more easily? How does the addition of the sodium hydroxide help with the aluminum nitride?

4. In what important detail does the process followed in this laboratory preparation differ from the commercial process of Serpek, and why would the former not be feasible on a commercial basis? Discuss the possibility of the process outlined in 5–A ever becoming a commercial process of "fixing" nitrogen.

5. What is the object of placing glass beads in the second U-tube?

6. Apply Question 2 under No. 5–A to aluminum nitride and aluminum carbide as well as to magnesium nitride.

7. Make for this preparation a calculation similar to that suggested by Question 5 under No. 5–A.
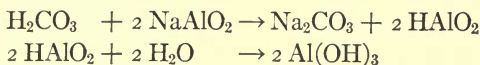
11–B. ALUM FROM SODIUM ALUMINATE
BY-PRODUCT, SODA CRYSTALS, $Na_2CO_3.10\ H_2O$

The solution left in the generator flask from the preceding preparation contained mainly sodium meta-aluminate,

$NaAlO_2$. Addition of an acid to this salt sets free the weak meta-aluminic acid

$$H_2CO_3 \ + 2\,NaAlO_2 \rightarrow Na_2CO_3 + 2\,HAlO_2$$
$$2\,HAlO_2 + 2\,H_2O \quad \rightarrow 2\,Al(OH)_3$$

The precipitated aluminum hydroxide serves as the starting point in the preparation of alum. Evaporation of the filtrate yields soda crystals as a by-product.

Read the discussion and procedure of No. 10, Alum from Cryolite, and note that we are here starting with the sodium aluminate solution which is the first intermediate product in that experiment. Note further that solutions of Na_3AlO_3 and $NaAlO_2$ differ only by the amounts of NaOH they contain.

Apparatus: large flask or bottle, 2 liters.
            1-hole stopper to fit mouth of same.
            2 pieces cloth filter 18 inches square.
            wooden stand 12 inches square for filter.
            agate pail.
            2 8-inch evaporating dishes.

Procedure. — To the residue in the generating flask in No. 11–A add 100 cc. of water, stir, and filter the solution through paper. Place the clear solution in the large flask or bottle and nearly fill the latter with water. Through the tight-fitting stopper lead a gas delivery tube to the bottom of the liquid and connect with the automatic carbon dioxide generator (Note 12, page 192, of Supplement). Loosen the stopper until all air is expelled, then close the flask and allow carbon dioxide to be absorbed until the solution is saturated. Tack one piece of the cloth filter to the wooden frame, allowing the middle to hang 4 inches lower than the edges. Lay the other cloth over the first one. Collect the precipitated aluminum hydroxide on this filter and catch the filtrate in a

clean agate pail. Wash the precipitate twice with hot water. Transfer the $Al(OH)_3$ to a dish and treat it with three times the volume of 6-normal H_2SO_4 which it took to neutralize the ammonia formed in 11–A. Warm the mixture for 5 minutes. If much undissolved substance is left, add 5 cc. more of 6-normal H_2SO_4, warm one minute, and continue with such additions until the solution is nearly clear. It is important to avoid adding more than a trifling excess of acid. For every 100 cc. of the 6-normal acid used in dissolving the $Al(OH)_3$ add 17.4 grams of solid K_2SO_4. Warm until this is dissolved. Filter the solution and bring it to crystallization as directed in No. 10.

Obtain soda crystals from the filtrate in the agate pail.

11–C. MODIFICATION OF 11–B.

BY-PRODUCT, GLAUBER SALT, $Na_2SO_4.10\ H_2O$

Follow the same procedure as in No. 11–B except in using H_2SO_4 instead of carbon dioxide in precipitating aluminic acid. An excess of carbonic acid does no harm, but an excess of H_2SO_4 dissolves an equivalent amount of $Al(OH)_3$. Before beginning operations, submit to an instructor your plan for telling just how much H_2SO_4 to add to completely precipitate the $Al(OH)_3$ without redissolving any. Obtain crystals of alum and of Glauber salt as the by-product.

23. LEAD NITRATE

Note to Procedure. — The solution which is set to crystallize should be slightly acid, — enough to redden litmus. If insufficient nitric acid is used, the excess of PbO dissolves in hot concentrated $Pb(NO_3)_2$ solution forming the basic salt $PbOH.NO_3$ which separates as a fine granular or flaky precipitate when the solution cools.

35. CHROMIC ANHYDRIDE, CrO₃

Materials: sodium dichromate, $Na_2Cr_2O_7.2H_2O$, 100 grams.
                concentrated sulphuric acid, 400 cc.
Apparatus: 8-inch evaporating dish.
              glass plate to cover the 8-inch dish.
              glass marble.
              unglazed porcelain plate.
              glass-stoppered sample bottle.

Procedure. — Dissolve the 100 grams of sodium dichromate in 250 cc. of water and filter from any sediment. Add rather slowly with constant stirring about half of the concentrated sulphuric acid until a slight permanent precipitate of CrO_3 is formed. Let the mixture cool for half an hour or longer, then add slowly, while stirring, the rest of the sulphuric acid. Let the mixture stand over night covered with a glass plate in order that the crystal meal may become somewhat coarser. In such a crystal meal standing in its saturated solution, the smaller grains dissolve and their material deposits out on the larger crystals. But even now the crystal meal will be rather fine and it will at first run through the filter; if, however, while waiting, the mixture is heated with stirring to 100° and allowed to cool slowly, and this process is repeated once or twice, a more satisfactory product will be obtained. To collect the crystals, use a suction filter, but place a small glass marble in the funnel instead of the usual plate and paper. If the red crystals at first run past the sides of the marble, pour the liquid in the bottle repeatedly back onto the filter until finally the filtrate runs clear (see last sentence of Note 3 on page 7). After draining the crystals completely and pressing the surface with a glass spatula, stop the suction and pour 15 cc. of the concentrated nitric acid so as to wash down the sides of the funnel and cover the surface of the product.

Stir up the product with this washing fluid for a depth of about $\frac{1}{2}$ inch. Suck dry and repeat the operation twice with 10 cc. of nitric acid each time. Finally transfer the product to an unglazed porcelain plate, place the latter on an iron ring and heat it by playing under it the burner held in one hand while with the other hand the crystals are continually stirred. Continue this operation, being very careful not to overheat, until nitric acid vapors cease to be given off. Transfer the product at once to a dry previously weighed glass-stoppered bottle.

gkt wst
pso

PERIODIC ARRANGEMENT OF THE ELEMENTS

M	—	Ra (226.4)	Act.	Th (232.4)	U+X₂	U (238.5)

* Between Cerium and Tantalum lie a number of elements which are very similar to each other in properties and which, together with Yttrium, Lanthanum, and Cerium, which they much resemble, constitute the so-called rare earth elements.